















# THE MANUFACTURE OF SULPHURIC ACID AND ALKALI

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VOLUME I.—PART III.



THE MANUFACTURE  
OF  
SULPHURIC ACID AND ALKALI  
WITH THE  
COLLATERAL BRANCHES

A THEORETICAL AND PRACTICAL TREATISE

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SULPHURIC ACID



PART III

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## PART III

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## CHAPTER IX

### THE CONCENTRATION OF SULPHURIC ACID

SULPHURIC acid, as obtained directly in the chambers (that is to say, from 106° to at most 124° Tw. strong), is sufficiently concentrated for many technical purposes; and where the acid is used up again for such purposes at the same works its further concentration is, of course, out of the question. This is the case, for instance, of several large industries having their own vitriol-works, such as the manufacture of superphosphate and of sulphate of alumina (concentrated alum). Even for making sulphate of soda from common salt it is possible to manage with acid of 124° Tw., although stronger acid is decidedly preferable; and in fact some alkali-makers work without any concentrating-apparatus, making their chamber-acid, as strong as possible. The want of concentrating-apparatus formerly excluded the application of a Gay-Lussac tower; and many works certainly did not possess such a tower. With the introduction of the Glover tower the state of things was changed, inasmuch as the manufacturers using this tower can concentrate all their acid to 144° or even 152° Tw. without any cost, and thus arrive at the same point as those who, not using that tower, concentrate their acid in lead pans. But since Glover towers are not universal, and since the acid passed through them is not suitable for all the uses of sulphuric acid (see p. 902), we must here describe the other concentrating-apparatus as well. These come into use especially where the strongest oil of vitriol is to be made, for which the Glover-tower acid is not very well adapted.

The vapour escaping from boiling dilute sulphuric acid consists entirely of water, and contains practically no sulphuric acid. The acid remaining behind will therefore become more

and more concentrated, without any material loss of acid, so long as a concentration of  $144^{\circ}$  Tw. is not exceeded. Walter (as quoted in Bode's *Glover Tower*, p. 17) found that the loss in concentrating acid in open pans up to  $144^{\circ}$  Tw. only amounts to 0.01 per cent. At the same time the boiling-point, which in the case of chamber-acid is about  $147^{\circ}$  C., gradually rises: that of acid of  $144^{\circ}$  Tw. is  $200^{\circ}$ ; that of acid of  $152^{\circ}$  Tw.,  $215^{\circ}$ . Beyond this the boiling-point rises very rapidly, and finally becomes stationary at  $338^{\circ}$  C., at which point not real sulphuric acid ( $\text{SO}_4\text{H}_2$ ), but an acid containing about 1.2 to 1.5 per cent. of water remains behind (p. 289).—In practice this limit is hardly ever reached; the heating is stopped when the remaining acid nominally shows  $168^{\circ}$  Tw.; often its real density amounts to only 1.830 or  $1.835 = 166^{\circ}$  or  $167^{\circ}$  Tw. A table of the boiling-points of sulphuric acids, according to their dilution, has been given above (p. 310).

The way in which sulphuric acid is concentrated depends, first, on the *material of the concentrating-vessels*. From what has been stated above (pp. 324 *et seq.*) it follows that sulphuric acid of  $144^{\circ}$ , or even up to  $152^{\circ}$  Tw., acts very little upon lead, even when hot; and so long as the acid has not to be stronger than  $144^{\circ}$  Tw., *lead vessels* are nearly always used, which offer the advantage that they can be made of any size, and that when they are worn out they can be very easily melted down and the material used over again. It is not advisable to carry on the concentration in lead pans above  $144^{\circ}$  Tw., because at that point the lead is much acted upon; and in no case can lead pans be used beyond  $152^{\circ}$  Tw., both because in that case the boiling-point of the acid too nearly approaches the temperature at which the lead begins to soften, and because the acid then acts too strongly upon it.

The *quality of the lead* used for boiling-down pans is of great importance; this subject has been treated, p. 324.

The further concentration of the acid must take place in vessels of glass or platinum, or in apparatus of peculiar construction, which will be subsequently described.

The concentration of sulphuric acid to  $144^{\circ}$  or to  $152^{\circ}$  Tw., where it is not effected in a Glover tower, is therefore always carried on in *lead pans*. These pans may be constructed in very different ways. They may either be heated by a direct

fire, and either from the top or from the bottom, or by steam, or by the waste heat of the pyrites-burners; and their construction differs accordingly, as will appear from the detailed description.

1. *Lead Pans heated from the Top.*

This is the appropriate mode of firing when the purity and especially the appearance of the acid are of less moment than a saving in fuel and the accomplishment of a large amount of work. The acid in this case is, of course, contaminated by the flue-dust, and is always more or less stained by sooty matters, whence its English name, 'brown vitriol,' has arisen. These contaminations are quite harmless when it is used for decomposing salt, for superphosphate, and for many other purposes.

On the other hand, the rate of evaporation in top-heated pans is very quick, because, first, the hot gas is brought into immediate contact with the acid, and can thus communicate its heat much better to the latter than when the two are separated by metallic plates; secondly, the vapours formed thereby are at once removed by the draught, which, as is well known from experience, very much assists the evaporation. Moreover, fired from the top, the pans, if properly constructed, are much less acted upon than when fired from below; especially the danger of being burnt through owing to the workmen's carelessness is much diminished.

Concerning the loss of acid in this style of evaporation no experiments have been published; probably it is somewhat larger than with pans heated from below, as the stream of fire-gases, acting upon the boiling acid, carries some of it away in the so-called "vesicular" form, *i.e.* as a mist of minute liquid drops, not in that of vapour, but more difficult to condense than the latter (*cf.* below).

According to this, pans with top-heat are especially suitable for alkali- and manure-works or for acid to be sold to the latter, but less so for sale-acid intended for other purposes. Such pans were at one time far more extensively used in England than pans with bottom-heat; but, like them, they have mostly become superfluous where Glover towers are employed. Such pans have been described by Godin (*Annales des Mines*, 1865, p. 344) and by myself (*Dingl. Polyt. J.*, cci. p.



352). In any case the lead must be protected from direct contact with the fire, or at least the pans must be cooled in such a manner that the lead cannot melt. The best way of doing this is to keep the pan always filled to the same level, nearly to its top, leaving only a sufficient margin to prevent any boiling-over. In ordinary work the acid is never drawn off altogether unless for repairs; but as the concentrated acid is heavier and sinks down, it is continually drawn off from the bottom, and fresh acid is constantly run in at the top, as long as the concentrating process goes on. Even then the empty portion of the pan has to be protected, especially at the fire-bridge; and, in many English works, for this purpose formerly a lead pipe was burnt on all round, through which ran a continuous stream of cold water. This contrivance cannot be highly recommended, because the pipe soon gets leaky. Moreover the raising of the water costs something; and therefore the following arrangement is preferable.

Fig. 370 shows a front elevation, Fig. 371 a cross section, and Fig. 372 a plan of a pan with top-heat. The fireplace, A (2 ft.  $\times$  4 ft.), is built up quite independently; its only connection with the pan B is by the arch *a*, and the fireclay slabs, *c*, 2 ft. long, lying on the fire-bridge, *b*; the slabs, *c* have a 6-in. hold on *b*; and as the space *d* between A and B is 1 ft. wide, they project 6 in. into B. The fireplace A is here shown as a plain grate; it might, of course, be more rationally constructed, and is now frequently replaced by a gas-producer. The air-channel, *d*, prevents any injurious effect of the heat of the fireplace on the pan, and we need only regard the flame itself in that respect.

The pan B is always made of a single sheet of lead, weighing from 15 to as much as 30 lb. per superficial foot; the corners are not made by cutting out, but by folding over, as shown plainly in Fig. 72. Since such stout lead cannot easily be bent cold, a small fire of shavings is made along the line marked out for the folding, of course taking care to avoid melting the lead; the lead then softens sufficiently to be bent with ease. The pan is placed on brick pillars, *e e*, standing quite free, so that the space between them and below the pan is accessible at any time. On the pillars strong wooden beams, *f f*, are laid; and across these 3-in. planks are placed close together; these are covered with a thin layer of sand, on which the pan itself is set. The pillars



FIG. 370.

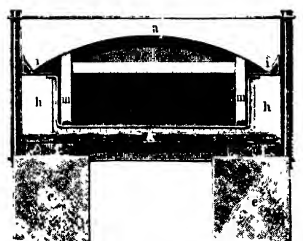


FIG. 371.

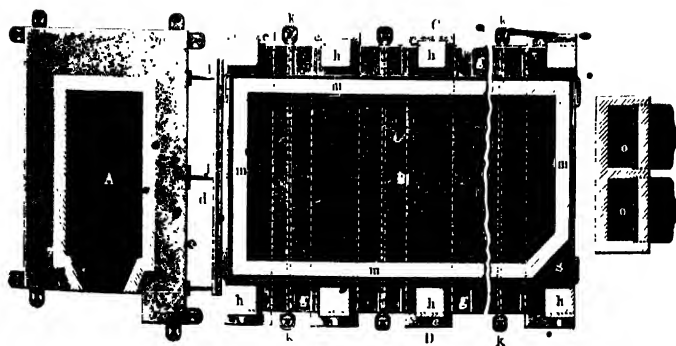


FIG. 372.

and beams project on each side 10 in. beyond the pan, and thus support small brick pillars, *h h*, 9 in. square, not quite touching the lead, and connected together at the top by cast-iron girders, *i i*. These have an angular section, and serve as springers for the arch *a*, which is thus quite independent of the pan. By themselves the pillars, *h h*, are much too weak to bear the side pressure of the arch; but this is kept up by the binding-rods, *k k*. The upper margin of the lead pan is bent round at a right angle and jammed in between the pillars, *h h*, and the girders, *i i*; in this way the sides of the pan are kept stiff. Next to the fireplace, where the pan becomes hottest and most readily gives way, it may be protected by iron rails and stays, *l l*.

A neater, but rather dearer, plan, shown in Fig. 373, is this:—Instead of the brick pillars, *c c*, shown in Fig. 372, cast-iron columns are provided, carrying, about halfway up, brackets, upon which metal plates for supporting the pan-bottom are laid. The columns are connected at the top by metal girders serving as springers for the pan-arch, and are kept together by bracing-rods.

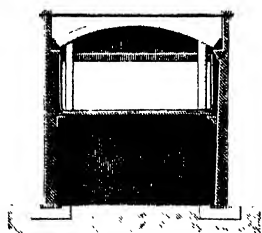


FIG. 373.

The proper protection of the pan from the fire is brought about by the dry wall, *m m* (Fig. 372), built up all round within the pan, of the best, hardest acid-proof fire-bricks or stoneware slabs. At one long sides this wall reaches up to the arch; at the fire-end it only reaches to the upper margin of the pan, and there carries the projecting fireclay slabs, *c*; at the chimney-end there are similar slabs, *n*, reaching up to the down-draught, *o*. The wall, *m m*, stands about 1 in. off the pan-sides, and has openings at the bottom, so that the acid can circulate freely. It is evident that the fire can nowhere touch the lead itself; and, moreover, the pan is also protected outside by the cooling action of the air; so that it cannot possibly melt or even soften. If the sides of the pan are to be stayed against bulging out, it should be done by open grids of cast iron, which do not prevent the lead from being cooled. The greatest danger of giving way exists at the fire-end, to which, certainly, great attention must

be paid. In the arch there are manholes,  $p\ p$ , and an inlet-pipe for acid, whilst the strong acid is drawn off by a siphon from the end  $s$ , left free by the arch; it is still better to attach to the bottom of the pan an overflow-pipe which rises to its top, and whose mouth can easily be narrowed according to requirement. The pan keeps better if the fresh, cool acid runs in at the part nearest the fire-bridge, whilst the strong acid is taken away at the opposite end of the pan, where it is coolest. The acid is always too hot to be used directly; and therefore it is run into shallow lead *coolers*, stayed by iron or wood frames, of which one is being filled whilst the contents of the other are being used. If the acid should not run off sufficiently strong, either the fire is increased or the supply of weak acid is diminished, or both.

The width of the pan is dependent upon that of the sheet-lead; if for the sides about 17 in. each are allowed, a width of about 4 ft. 11 in. generally remains. The length is always much more considerable, rarely below 20 ft., but sometimes as much as 33 ft. The longer the pan, the better the fire is utilised. The consumption of fuel is always much less than in the case of pans with bottom-fires; Bode estimates it at from 10 to 12 per cent. of the strong acid, but I can report from a thoroughly trustworthy source that in properly constructed pans of this kind only 2 or 3 parts of coal are required to make 100 parts acid of  $142^{\circ}$  Tw. from chamber-acid of  $110^{\circ}$  Tw. The repairs of a properly constructed pan of this kind are much less than those of a pan with bottom-heat (as they always are in analogous cases); and the work done is much larger for an equal area. A pan of 4 ft. 11 in. width by 33 ft. length was sufficient, in my experience, for boiling down 80 tons of acid of  $144^{\circ}$  Tw. per week, from chamber-acid of  $116^{\circ}$  to  $124^{\circ}$  Tw.

These pans were described exactly as above in the first edition of this book (1879), and that description was taken from the factory managed by myself as early as 1866; of course they were known previously to that, although I am not aware who first constructed them. But it would appear that the knowledge of this fact has been forgotten, for when the Hasenclever modification of the Deacon process (B. P. 3393 of 1883, described in Vol. III. of this work) was introduced into England, the pans employed in that process for the purpose of

reconcentrating the sulphuric acid, diluted in the process of purifying impure hydrochloric acid, were styled "Hasenclever pans," although they are constructed exactly as shown above, with unessential modifications, *e.g.* a cast-iron grid running along the sides of the pans, instead of the pillars *h h*, Fig. 72. These "Hasenclever pans" have in the course of years acquired an unenviable notoriety in consequence of the amount of acid carried away into the chimney, probably not at all in the state of vapour, but of a "vesicular" mist produced by the boiling of the acid in a stream of fire-gases. Constant complaints have been made in that direction, and especially the *35th Report on Alkali, etc., Works*, swarms with them. In the *36th Report*, however, for the year 1899, p. 18, it is remarked that at one works a very great improvement had been effected, not that the "total acids" were very materially reduced, but that they are discharged in a less vesicular physical condition, so that their density is less and they do not, as is otherwise the case, fall heavily among the neighbouring streets without diffusion and dilution in heavy weather. This improvement has been brought about by firing with gas-producers. The primary air is carefully regulated, and the secondary air is heated up by what would otherwise be lost by radiation. This secondary air is introduced into the (sufficiently large) combustion-chamber at such a point that immediate contact of the flame with heated acid is avoided as much as possible.

- Clough (*American Patents, Official Report*, i. p. 495; iii. p. 166) has proposed a similar apparatus for concentrating the acid up to 1.50  $\gamma$ . His pan is protected from the fire, inside by a wall and outside by cold water contained in an iron jacket. This can hardly be put into practice, because the loss of acid vapours would be too great, and the pan would not stand the wear and tear, in spite of the water-jacket.

Grosse-Leege (Ger. P. 176370) introduces the current of hot air or heating-gases tangentially to the inner side of a round evaporating-dish, close to the surface of the liquid, so that the gases take a spiral circuit above the acid and ultimately escape through an exit-pipe in the centre of the arch. Several special modifications of this arrangement may be carried out, and a series of dishes may be employed in the well-known manner. The hot air, charged with vapours, is carried off from each

single dish, without getting into contact with fresh vapours within the apparatus, either into the open air or into a special flue.

According to the *38th Alkali Inspector's Report*, p. 75, the firing by means of producer-gas, while keeping the acidity of the escaping gases more constant, had failed to reduce the amount of acidity, as the fire-gases leave the pans at far too high a temperature. The Inspector strongly recommends to abandon the ordinary system of surface-heat evaporation in favour of the Kessler furnaces (*cf.* pp. 1141 *et seq.*).

The *42nd Report on Alkali Works* (for 1905), p. 20, states that recently less nuisance had resulted from the surface-heat system of concentration than in former years, owing to the fact that the discharge of the acid-bearing vapours no longer takes place from very low chimneys, but through high stacks.

## 2. Lead Pans heated from Below.

These pans are mostly made of much smaller size than those with top-heat; the essential reason of this is the different wear and tear which they suffer according to whether they are more or less exposed to the fire; moreover the concentration in this case is very regular, the pans always being arranged in sets, so that the weak acid flows in at one end of the set and runs over from one pan to another till it runs off sufficiently strong at the other end of the set, in order to be used up or sold, or to be further concentrated in platinum vessels. Sometimes, however, long pans made in one piece are used, especially in England. In that case the first part, nearest the fire, is protected by an arch, the larger part of the pan-bottom behind this by fire-clay slabs or metal plates. Such a pan is shown in our second edition, pp. 664 and 665.

The metal plates are sometimes covered by a thin layer of sand, in order to communicate the heat evenly to the pan; but this greatly hinders the heat-convection. The pan is stiffened inside by iron stays covered with lead; and it is covered by an arch to carry off the vapours into the open air or into the chambers—the latter rarely.

On the Continent small pans are very generally used, of 5 to 7 ft. length and width, and from 12 to 16 in. depth, of which from four to six form a set. They are made of 15 to

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18-lb. lead, mostly by bending up the sides and folding over (not cutting out) the corners. Sometimes such pans, instead of being made of sheet-lead burnt together, are *cast*, about  $\frac{3}{4}$  in. thick. They are in that case exposed to the fire directly, without interposing iron plates. This plan cannot, however, be recommended. Such cast-lead pans, being much thicker, are dearer than those made of sheet-lead; and they are much more liable to have unsound places, which are very soon eaten through. They are often set in steps, each pan about  $2\frac{1}{2}$  in. lower than the preceding one; in other cases, however, they are placed with their bottoms at the same level, but are made of different depths—the pan which receives the weak acid being the deepest (16 in.), and each following one a little less, the last pan (for strong acid) being 12 in. deep. In this way the acid can also flow from one end of the set to the other. At the Oker works there is a long pan divided by partitions into seven compartments of equal height and level; the fire-grate is in the centre of one side; and the flame first passes in the centre to the back, and then returns at both sides to the front of the pan.

The acid is sometimes carried over from one pan into the next by continuously acting siphons. But as such siphons frequently cease to act in consequence of air getting in, owing to the slow current and the small difference of level, an overflow-pipe ought always to be provided to prevent the pans from running over. It is even preferable to replace the siphons altogether by overflow-pipes, which take the acid from the bottom of one pan and allow it to run on to the top of the next one; but this arrangement requires the work of a very good plumber to last without continual repairs. The chamber-acid is constantly running into the first pan in a regulated stream; and the strong acid runs off from the last pan without any further interference, the supply being so regulated that the proper strength is obtained.

The pan-bottoms are always stayed and protected from the direct action of the fire by cast-iron plates, which are thicker at the fire end than further off—say, decreasing from 2 in. down to  $\frac{3}{4}$  in. Frequently the first pan, below which the fire-place itself is built, is protected by an arch. MacDougall (B. P. 21778 of 1895) employs perforated cast-iron plates for

supporting the bottom, preferably in the shape of a grid with longitudinal and transverse rills, leaving diamond-shaped holes. This plan indeed, according to *Alkali Report*, No. 31, p. 54, prevents a local overheating of the pan-bottoms, which readily occurs with solid cast-iron plates, and the pans do not show any buckling even after prolonged use.

Carulla (*J. Soc. Chem. Ind.* 1893, p. 15) interposes a copper plate  $\frac{3}{4}$  in. thick between the lead and the ordinary solid 1-in. cast-iron plate, which, owing to its good conduction of heat, very efficiently prevents local overheating of the lead without interfering with the transmission of the heat.

Opinions differ as to the way in which the firing of the pans should be arranged. Formerly the usual arrangement was that of putting the fireplace under the strong pan, and allowing the fire to travel towards the weak pan, which receives it last of all. In this case the greatest heat exists where it is most required, since the concentration of the strong acid is more difficult and its boiling-point higher, and since the fire-gas eventually comes into contact with cold acid. When the pans are set terrace-fashion, the fire takes its most natural direction, viz. upwards.

Practice has, however, mostly decided for the opposite plan, namely, arranging the fireplace under the weak pan, so that the strong pan is furthest from the fire. In this case the strong pan, which is otherwise worn out very quickly, suffers hardly more than the others, and the evaporation still goes on at a satisfactory rate, although there may be a little more fuel used than with the old arrangement, which is undoubtedly more rational as an evaporating-plant, but less adapted to the special needs in this case.

Bode cites the temperature and strength of the acid in a set of six pans, where the fire travelled in the same direction as the acid, viz. :—

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.	5th pan.	6th pan.
a. Temperature 25°	112°	150°	160°	148°	145°	143° C.
Strength 110°	113	120	128	134	140	144 Tw.
b. Temperature 24°	110	145	156	145	142	142 C.
Strength 110°	113	118	126	134	140	144 Tw.



## 1090 THE CONCENTRATION OF SULPHURIC ACID

Here the hottest pan is the third; so that the fire is badly utilised. According to his experience this set required 20 parts and upwards of coal to produce 100 parts of acid of  $144^{\circ}$  Tw.; whilst in the set illustrated below (Figs. 374-377), where the fire meets the acid, only 15 to 16 parts of coal were used (on the average of several years). For each ton of strong acid, in twenty-four hours, about twenty superficial feet of pan-bottom may be reckoned; the whole set, therefore, furnishes  $6\frac{1}{2}$  tons every twenty-four hours.

Bode gives the temperatures and strengths of the acid during concentration in pans with the old style of setting as follows:—

Set of four pans :

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.
Temperature $20^{\circ}$ . . .	52	78	120	$138^{\circ}$ C.
Strength 106 . . .	...	.	...	144 Tw.

Set of three pans heated by the pyrites-burners :

Acid running in (heated previously).	1st pan.	2nd pan.	3rd pan.
Temperature $70^{\circ}$ . . .	105	125	$147^{\circ}$ C.
" 57 . . .	92	106	125 C.
Strength 106 . . .	.	.	144 Tw.

According to Hasenclever, it is well to regulate the working of the pans by thermometers, in order to avoid any risk of damaging them.

Figs. 374 to 377 represent the set of pans designed and constructed by Bode, where the fireplace is outside, in order to save the first pan. From this, by means of a pan-area of 118 superficial feet and a fire-grate of  $6\frac{1}{2}$  superficial feet, 5 tons of strong acid could be produced every twenty-four hours, with a consumption of 12 to 14 per cent. of Silesian coal. Figs. 269 to 272, pp. 669 and 670 of our second edition, show a modification in which a Fairbairn's double fireplace is used. In all of these the strong pan is placed over the fire, as usual formerly, whilst at the present day the order would be reversed.

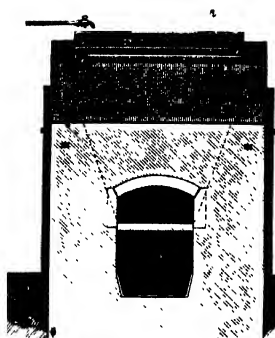


FIG. 374.

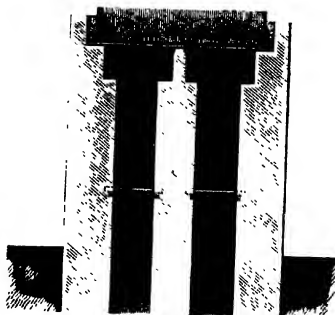


FIG. 375.

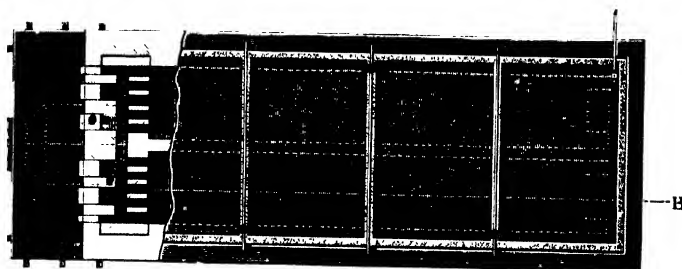


FIG. 376.

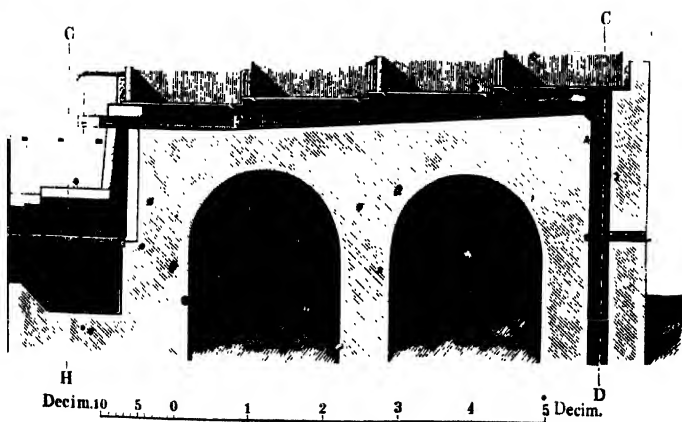


FIG. 377.

According to Scheurer-Kestner (Wurtz, *Diction. de Chim.*, iii. p. 159), four pans, 6 ft. 6½ in. by 3 ft. 11 in. each, permit the concentration from 109° to 152° Tw. of sufficient acid to produce 3 tons of concentrated acid daily, with a consumption of no more than half a ton of coals.

Bode calculates the cost of erecting a concentrating-apparatus like that shown in Figs. 374 to 377 at £150, and that of keeping it in good working order at 12 per cent. per annum. The cost of the concentration itself, reckoning coals, wages, and wear and tear, in four actual cases, amounted to from 2s. 3½d. to 2s. 8d. per ton.

Junge (*Jahresber. Berg- u. Hutten. Sachsen*, 1892; *Z. angew. Chem.*, 1893, p. 61) describes the bottom-fire pans as used at Freiberg. They are about 6 ft. 6 in. long, 3 ft. 3 in. wide, and 8 in. deep. They are supported by ⅞ in. cast-iron plates and are arranged in tiers, the fireplace being underneath the strong bottom pan and the acid running in at the top pan. These pans furnish a uniformly strong acid, and consume only two-thirds as much fuel as the steam-pans. They suffer, however, under the disadvantage that the first strong pan is quickly worn out. [It is strange that Junge does not even mention the arrangement, represented as the only rational one on p. 1089, in which the fireplace is situated underneath the *weak* pan, in order to lessen the wear and tear.] Sometimes the pan-bottom is suddenly destroyed, the cause of which is unknown. [The explanation of this phenomenon is given by the investigations of Lange and Schmid, p. 325; or else by the cause mentioned on p. 1066.] In normal work the temperature of the acid running off is 200° C. [This is much higher than has been hitherto observed, and this may explain the great wear and tear.]

Very good results have been obtained with a system in which the fireplace is arranged underneath a platinum dish, covered with a water-cooled dome and protected by a brick arch below. From this the fire passes underneath the lead pans, in which the acid thus never exceeds 60° C. or 58° B. The sudden destruction of the first pan never happens in this case. After fifteen to twenty weeks' use it begins to leak slightly, so that the acid can be drawn off before any trouble arises. The first pan now lasts three or four months, the

second two or three years, the others five years, and they can be replaced within twelve hours at a trifling cost. This apparatus, inclusive of the platinum dish, costs about as much as the steam-apparatus described, pp. 1098 *et seq.*, inclusive of the steam-boiler; it requires much less space, is quite as safe, and furnishes a stronger and more uniform acid, with a much smaller consumption of fuel.

The Zeitzer Eisengiesserei (Ger. P. 99768; *Fischer's Jahresber.*, 1898, p. 328) employs a cylinder of antimony-lead, heated inside by fire-gases (? *cf.* p. 1101), and fitted on the outside with a number of antimony-lead dishes arranged so that the acid overflows from each dish to the lower one.

Wolters (B. P. 18831 of 1893) carries the evaporation in lead vessels beyond the usual extent, preventing the action of the acid on the lead by saturating the acid with lead sulphate. An excess of this is put in and is kept in suspension by mechanical stirring. Most of the dissolved lead sulphate crystallises out on cooling and can be used over again.

### 3. *Lead Pans fired by Waste Heat.*

In factories possessing platinum apparatus for making acid of 170 Tw., the fire of these can never be so far utilised that the waste heat could not be employed for heating lead pans; and this is actually done in most practical cases.

Much more generally applicable, and quantitatively more efficient, is the utilisation of the waste heat of pyrites- or sulphur-burners for concentrating chamber-acid. Where there is no Glover tower (which utilises that waste heat in a different and even more thorough manner) the above process is most rational, since here also the same operation which produces the concentration of the acid fulfils another useful function, that of cooling the burner-gas before it enters the chambers.

The pans used in this case are generally made exactly like those for concentrating with bottom-fires. They are mostly placed on the pyrites-burners themselves: they must not, however, be set directly upon the burning pyrites, nor even with merely a metal plate between, but must be separated from it by a brick arch. In most cases a gas-flue is placed immediately over the burners, serving at the same time as a dust-chamber, on the top of which the acid-pans are placed (see the diagrams of Malétra

burners, pp. 465 *et seq.*). Sometimes, from fear of leakage from the pans into the burners, they are not placed over these, but upon a continuation of the gas-flue. Haseklever even advises building a second gas-flue, to be used during the time when the pans have to be repaired. The heat of the kiln-gas is not in this case turned to account so well as if the pans stood directly upon the burners; and the latter plan can be employed all the more safely, if the danger of leakage into the burners is avoided by providing the metal plates, on which the pans rest, with a flange all round and an outflow for any acid collecting in it, like those used in nitre-ovens. Leakages occur also less easily where the pans are very shallow, so that the depth of acid is only a few inches. But, on the other hand, it has been noticed that sometimes, especially in the case of poorer ores, the pans on the burners withdraw too much heat from these to be conducive to good burning. For this reason they have been abolished at the Oker Works.

Whilst at some places such pans on the top of the burners concentrate all the chamber-acid from  $112^{\circ}$  to  $140^{\circ}$  Tw., at others they do not get so far, and they must use a small coal-fire for completing the concentration.

The diagrams, Figs. 378 to 384, represent pans designed by Bode, together with the pyrites-kilns used by him. The apparatus shown here belongs to a set of chambers of 40,000 cub. ft. capacity; and each burner receives daily 16 cwt of Westphalian pyrites containing 42 per cent. of sulphur. The grate of each burner has a surface of 34.4 sq. ft.; the grate-bars are elliptical, 3 in. by  $1\frac{1}{2}$  in., each of them movable; the arch is 4 ft. 4 in. above the grate, with a spring of 7 in. The diagrams show how each burner can be cut off separately. The pans are 6 ft. 3 in. by 4 ft. 2 in. by 1 ft. 2 in., made of sheet-lead weighing  $8\frac{1}{4}$  lb. per superficial foot. They supply daily, when  $1\frac{1}{2}$  tons of pyrites is burnt, altogether 2 tons 5 cwt. of acid of  $144^{\circ}$  Tw. (that is to say, 5 cwt. in excess of the make of the chambers); but as at the same time from 15 to 18 cwt. daily have to be evaporated for the Gay-Lussac tower, the excess causes no inconvenience. Each year three new pans used to be put in, a pan never being left until actually burnt through, but replaced as soon as the lead had become too thin—a plan most decidedly to be recommended in every case.

The renewal only refers to the strong-acid pans; those for weak acid are hardly injured at all. The former are therefore much

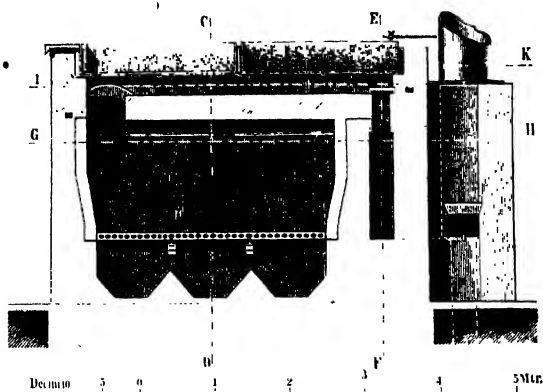


FIG. 378.

better made of thicker lead, say 30 lb. to the superficial foot, in which case they last for about two years.

The cost of concentration with such pans only amounts to a

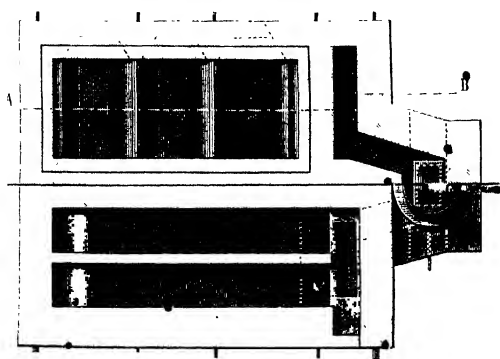


FIG. 379.

small fraction of the wages of the burnermen, in addition to the expense of renewing the pans; Bode calculates it, for a special case, at 4½d. per ton of strong acid; for less favourable cases he estimates it at 6d. to 9d. per ton.

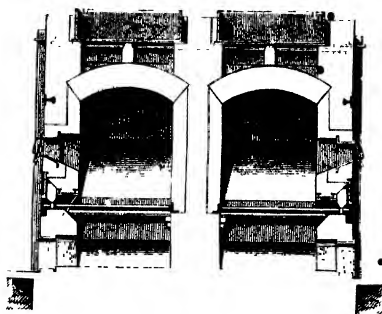


FIG. 380.

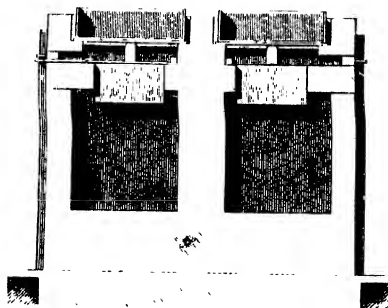


FIG. 381.

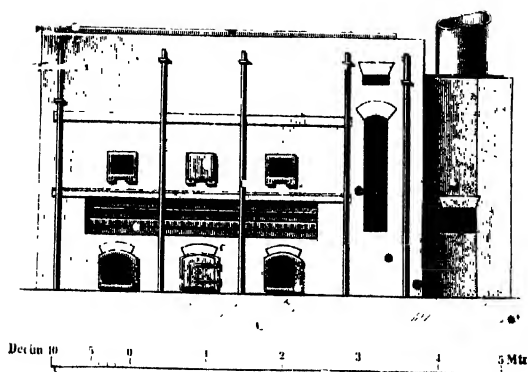


FIG. 382.

Some manufacturers and managers assume that it is irrational to concentrate the acid on the top of the burners, because the trouble and incessant repairs caused by leakages are believed to be far worse than the expense of heating the pans by a separate fire. To this I must oppose that I know of

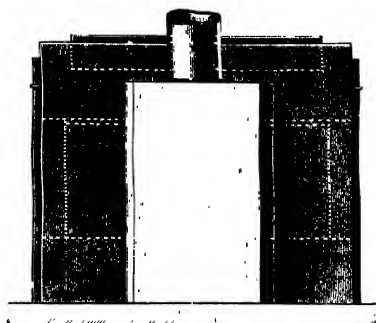


FIG. 383.

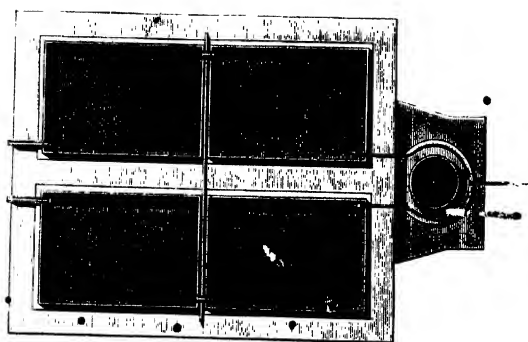


FIG. 384.

a great number of works where all the pyrites-kilns are provided with pans placed on the top, and where this arrangement has been at work for many years (in a special case I can speak of thirty years) without giving any trouble whatever. This is proof conclusive that the troubles from leakages complained of



are caused by a wrong setting of the pans or else by keeping too deep a layer of acid in them (the latter being a very important circumstance). Where they are not placed directly over the kilns, but over the gas-flue (this flue is mostly itself placed on the top of the kilns), and where they are properly protected below by metal plates and a thin sand-bed, they stand as long as may be desired, provided that only a shallow layer of acid is kept in them. Indeed, it may be said that such an arrangement of utilising part of the heat of the pyrites-kilns, and allowing the other part to act in the Glover tower, is decidedly the best and cheapest plan, where the acid is required of purer quality than can be obtained from the Glover tower; the latter then acts much more as a denitrator than as a concentrator, and the acid produced in it is principally used for the Gay-Lussac tower, the surplus only being used or sold for other purposes.

In the case of *brimstone-burners* it is equally possible and altogether rational to employ their heat for concentrating sulphuric acid. In this case the burners are not covered with an arch, but with 1-in. cast-iron plates, and shallow lead pans are placed immediately above these. Such an arrangement is shown in Stahl's sulphur-burners (*supra*, p. 398); in H. Glover's burner (p. 403) it is combined with a platinum dish. This partial utilisation of the heat of the gases does not at all prevent their employment for working a Glover tower. I have seen this combination carried out in several places in America, where the Glover tower denitrates and concentrates all the acid destined for working the Gay-Lussac tower, while the acid for sale is concentrated up to 140° Tw. in lead pans placed on the top of the brimstone-burners. The Glover acid in these cases still issues about 150° Tw. strong, and 126° to 130° C. hot.

#### 4. *Concentrating-pans heated by Steam.*

According to Hasenclever (*Ber.*, v. p. 504), the idea of concentrating sulphuric acid by means of indirect steam was first proposed by Carlier, the manager of Messrs Curtius' chemical works at Duisburg.<sup>1</sup> After several trials at that works they ultimately employed wooden tanks lined with lead, 15 ft. square,

<sup>1</sup> He seems to have overlooked Smith & Savage's Amer. P. No. 41647 of 1864.

on the bottom of which lie two lead coils, each of 150 ft. length,  $1\frac{1}{4}$  in. bore, and  $\frac{1}{4}$  in. thickness of lead, for conveying steam of 45 lb. pressure. The bottom of the pans is shaped like a truncated pyramid, for the purpose of more easily running off the condensed water; so that the tanks are 2 ft. deep in the centre, 1 ft. deep at the sides. The two ends of each steam-coil are connected with a lower-placed steam-boiler, into which the condensed water continually flows. When the acid has arrived at  $140^{\circ}$  Tw., it is run into a leaden tank, through which a lead coil passes; the fresh chamber acid runs through this coil; and, in cooling, the strong acid gets a preliminary heating. With the above apparatus 5 tons of strong acid can be obtained from chamber acid of  $100^{\circ}$  Tw., every twenty-four hours, by the consumption of 9 cwt. of coals. The steam-boiler requires only as much fresh water as is lost through leakage at the flanges, etc. It is advisable to place a wooden hood over the steam-tank, to prevent any danger from acid being splashed about in case of a steam-pipe bursting. Owing to the low temperature, no acid at all is evaporated; the process is very cleanly, and economical as to consumption of fuel and labour. This Report of Hasenclever is fully borne out by Bode. Hasenclever (*Hofmann's Report*, 1875, i. p. 185) states the corrosion of lead to amount to 0.44 lb. of lead per ton of acid. The steam-pipes are mostly acted upon in the places where they dip into the acid, because the dust accumulating there raises by capillarity some acid above the level of the remainder, and this becomes too highly concentrated by evaporation. Since a lead jacket has been burnt to the steam-pipe at the place in question, the above drawback no longer exists.

Figs. 385 and 386 represent a similar apparatus, copied from Bode's *Gloverthurn*, p. 27. The tank here measures 10 ft. 6 in. by 14 ft. 9 in. at the surface, 1 ft. 4 in. depth in the centre, 1 ft. at the sides, is heated by steam of 37 lb. pressure, and supplies in twenty-four hours 5 tons of acid of  $114^{\circ}$  Tw. with a consumption of 10 cwt. of Silesian coal. At some works Bode found a consumption of only 8 cwt.; at others, however, from 15 to 18 cwt. of coal for the same quantity of acid.

The steam-coil must have a valve both where it enters and where it leaves the pans, which should admit of being closed from a distance in case of the coil bursting. Both the coil and the

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return-pipe for condensed water (for which a steam-trap should be provided) must be placed in such a way that the water cannot cause a stoppage anywhere. The lining lead weighs from  $6\frac{1}{2}$  to 10 lb. per superficial foot. The whole cost of concentration by these pans, including labour, wear and tear of the pan-lead and of the steam-boiler and coils (using 9 cwt. of coals for 5 tons of vitriol), is calculated by Bode at 1s. 8d. to 1s. 10d. per ton of strong acid.

It is very important to place the outlet for acid in such a

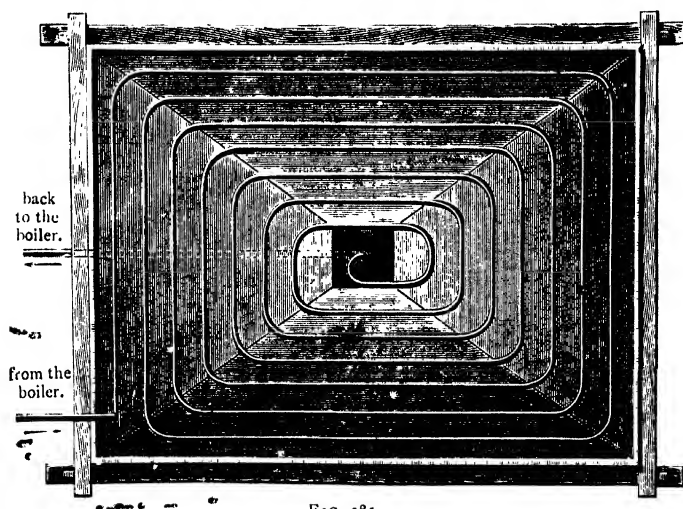


FIG. 385.

position that the steam-coil remains completely covered when running off the acid, and is never exposed to the air, which would greatly injure the lead. After a year's work the steam-coil ought to be replaced by a fresh one, even if not showing any outward damage.

Some manufacturers avoid running the condensed water back into the boiler, lest the latter should be damaged by any acid getting into it, or even caused to explode; in such cases the above-mentioned larger quantity of coals is used. Bode points out that there is no danger of acid getting into the steam-boiler, because in case of the steam-boiler bursting the

steam blowing off will prevent the acid from entering the boiler. The return-pipe must not end below the water-line, but in the steam-dome.

Dr Stahl recommends employing steam of no more than 30 lb. pressure, in order to reduce the danger of bursting pipes to a minimum.

The process of concentration by steam certainly furnishes the purest acid, and was formerly considered cheaper than the other plans, excepting the Glover tower or the pans placed on the pyrites-burners. It has been introduced into several

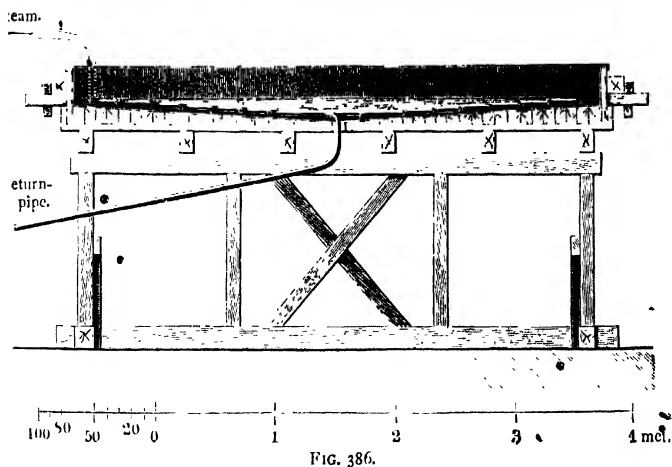


FIG. 386.

German works, but latterly the reports on the economical working of that plan have not been so favourable as formerly. At Stolberg this plan has been given up again as being too costly.

Several new steam concentrating-apparatus for sulphuric acid have been introduced in connection with ice-making apparatus, all of them founded on the principle of the multi-tubular boiler. We mention of these the apparatus of Kux (Ger. P. 31277), Fig. 387. The upper part *a* and lower part *b* are connected by many lead pipes, *c*; through these and the outside pipe *d* the acid circulates. The whole system is surrounded by a shell *e*, into which steam is introduced through

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*f*, the outlet being at *g*. The thin acid is introduced at *h*, the concentrated acid flows away at *i*; pipe *k* takes away the vapours, and a water-pipe *m* with an inner pipe *l*, perforated by many holes, condenses any acid carried over.

Egells (Ger. P. 31620) describes a very similar apparatus, in which the tubes are placed in a horizontal direction, and special precautions are taken against any sagging of the tubes *c*. Kurtz (Ger. P. 37713) employs lead pipes provided with inner iron pipes. A combination of a leaden pan with evaporating-

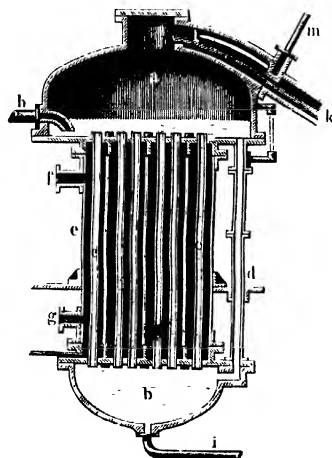


FIG. 387.

worms placed sideways of it forms the subject of a patent of the International Vacuum-Eismaschinenverein (Ger. P. 38015; *Fächer's Jahresber.*, 1887, p. 508).

Kurtz (Ger. P. 38018) describes a steam-heated pan with counter-current.

Solvay and Co. (Ger. P. 54730) promote mechanical circulation in such a pan by a mechanically driven screw-wheel.

Junge (*Jahresber. Berg- und Hütten. in Sachsen*, 1892, *Z. angew. Chem.*, 1893, p. 61) describes in detail the steam-heated acid-pans employed at Freiberg. They are flat-bottomed boxes, lined with 5 mm. lead, about 10 ft.  $\times$  4 ft. 3 in. and 14 in. deep, with a coil of lead pipe, 1  $\frac{1}{8}$  in. bore,  $\frac{5}{16}$  in. thick, 184 ft.

long, resting on loose pieces of lead-piping. Six such pans are combined in a set, communicating by overflows; the acid runs in at one end and out at the other. The steam-pressure is not allowed to exceed  $2\frac{1}{2}$  atm. The temperature rises in the first pan to  $125^{\circ}$ , and does not go above  $128^{\circ}$  in the last. The strength of the acid (entering at  $51^{\circ}\cdot4$  B $\acute{e}$ .) in the six pans is respectively:  $53^{\circ}\cdot9$ ;  $56^{\circ}\cdot1$ ;  $57^{\circ}\cdot4$ ;  $58^{\circ}\cdot6$ ;  $59^{\circ}\cdot4$ ;  $50^{\circ}\cdot2$  B $\acute{e}$ . Hence a comparatively low pressure, far below the boiling-point of the acid, suffices for concentration; but this involves slower work and much more plant than concentration by direct firing. The cost of repairs is slight so long as the apparatus is new, but subsequently it is very considerable. The thickness of the steam-coils corresponds to a strain of 60 atm. in the cold; in spite of this they later on became bulged out and burst with a pressure of only  $2\frac{1}{2}$  atm. This is caused partly by the action of steam from within and hot acid from without, partly by the gradual diminution of the tensile strength of the lead used at that high temperature. Lead alloyed with  $1\frac{1}{2}$  per cent. antimony (hard lead), cannot be used, as it is quickly destroyed by hot sulphuric acid (*cf.* pp. 326 and 1104). This occurs chiefly in the places where the hard lead is in contact with soft (pure) lead and galvanic action sets in; but this is noticed only at higher temperatures, not with apparatus worked at the ordinary degree of heat. The steam-pans are gradually very much impaired in their efficiency by lead-mud, etc., settling between the coils; they then furnish less and weaker acid. Hence their use cannot be recommended, except where it is absolutely necessary to avoid any injury to vegetation, which is certainly altogether excluded here, as well as any loss of acid. But they are far more costly, both to erect and to work, than directly fired pans.

Evers (Ger. P. 176369) concentrates sulphuric acid (or nitric acid, etc.) in a vessel, on the bottom of which there are two coils, arranged concentrically in such manner that the heating-liquid flows through them in succession.

*Lead vessels for higher concentration than up to  $152^{\circ}$  Tw. can be used only by the application of a vacuum and will be mentioned in a later part of this chapter.*

*Quality of the Lead for Sulphuric Acid Pans.*

W. B. Hart, in *J. Chem. Soc.*, 1907, pp. 504 to 511, discusses in detail the influence of the physical condition, and chemical constitution of the lead on its durability for pan-concentration of sulphuric acid. He summarises his conclusions as follows. Lead failure can originate both from chemical composition (due to imperfect desilverisation or final refining, or to the presence of bismuth, or dross, or oxide) and from the physical condition. The effects of impurities are as follows:—

1. Physically, by the formation of alloys of low fusibility and consequent local perforation of the lead, most likely owing to the presence of bismuth or tin. By leakage and consequent concentration in such cases the action may extend even to the lead itself.

2. Chemically, at certain stages of the concentration, by strong sudden action, due to the presence of Al, Sn, or Zn, and by slow action to the presence of bismuth.

3. Chemically, by the increased action of the acid on the lead, owing to the physical condition of the impurity, especially Zn.

4. Slow electrolytic action may set up with the deposition of certain impurities, which may accumulate and then set up physical and chemical action.

5. Antimony may have a strong and harmful chemical action, whilst copper, arsenic, and silver have little effect, and copper may even be useful under certain conditions. By constant use copper will be slowly dissolved and its corrective effect on other impurities is then diminished or lost, so that, e.g., bismuth can exert its influence more freely. This explains the failure of lead pans which have previously given good results for a long period.

6. Pure lead, under normal pan conditions, is undoubtedly less affected than the impure metal.

Failure from physical conditions may be due to faulty remelting of the lead, by use of unsuitable casting temperatures, and by severe pressure in the rolling operation, in the following way:—

1. Production of a loose crystalline structure, by casting the metal at too high a temperature, causing leakage and concomitant results.

2. By severe pressure during rolling, production of a lead surface more susceptible to attack, either temporary or constant.
3. Strong acid action in the temporary, physically altered form of lead, before the annealing effect can take place, explains the failure of pans which have been in use for a limited period.
4. The effect of altered physical condition will extend even to lead of an exceptionally pure chemical composition.

*Concentration to 144° Tw. in Platinum Vessels.*

*Concentration in platinum dishes*, in Faure and Kessler's apparatus (p. 1142).—The inventors state that 7 parts of coal suffice for obtaining 100 parts of acid of 143° Tw. from acid of 106° Tw., of which quantity  $4\frac{1}{2}$  to 5 parts of coal may be deducted if the steam be used for the acid-chambers. The same might be done in any other plan; but it rarely is done, because too much air is carried along with the steam. According to Bode, in reality  $10\frac{1}{2}$  parts of coal are used, the warm water being utilised for feeding a boiler. This system, applied to concentration up to 144° Tw., does not seem to be able to compete even with the steam-pans, let alone the pans heated by pyrites-burners or the Glover tower, least of all if the cost of plant be considered.

*The Last Concentration of Sulphuric Acid.*

We have seen that we cannot carry on the concentration in lead pans beyond 150° or, at the outside, 152° Tw., the latter not without a somewhat strong action upon the lead. In the Glover tower it is possible to go rather further, as its lead is protected by the lining so as to be acted upon very slightly; the acid does not come into contact with the lead, but only with the flints, bits of pottery, etc., and arrives at the bottom with a temperature of about 130° C.; so that even the bottom of the tower, which is made very strong, is not sensibly acted upon. In fact those manufacturers (being the majority) who work the Glover tower with hot gas from rich ores, and get their chamber-acid up to 120° to 124° Tw., regularly attain a concentration of 152° Tw., and in some cases even 156° or 160° is reached. The latter is the exception, and already dangerous to the tower; if it were not so, the concentration by hot kiln-gas in the Glover tower (of course modified to some extent) would be the cheapest plan for the last concentration of the



acid, because then the escaping gas goes into the chambers and is not lost at all. We shall see below that this has been indeed attempted.

Concentration beyond the point attainable in lead pans or in the Glover tower is a much more difficult task, involving incomparably more expense than the first concentration. Since the attempts to concentrate the acid up to  $170^{\circ}$  Tw. by means of cooled lead pans with top-heat (Clough), or by a vacuum (Keller, De Hemptinne), or in towers filled with pebbles and heated directly by heating-gas (Gossage), or other ways had not been successful, and since cast iron is not easily available below the point to which "rectified O.V." is brought in ordinary work, recourse was formerly universally had to apparatus made of glass or platinum, of which the former have the drawback of very restricted size and great liability to breaking, the latter that of being very costly without being proportionately durable. These circumstances make their application both expensive and troublesome.

By far the largest quantity of acid is used of no higher strength than is attainable in lead, mostly even rather weaker. For making sulphate of soda, the acid is never taken stronger than  $144^{\circ}$  Tw., generally only  $140^{\circ}$  Tw. The English manufacturers as a rule dilute their Glover-tower acid down to this point with chamber acid; or they only make as much acid of  $152^{\circ}$  in the Glover tower as is required for working it, and keep the remaining acid weaker by running more chamber-acid through the tower. For the manufacture of superphosphate the acid is mostly employed even in a weaker state; and this, together with the sulphate of soda, consumes most of the total quantity of sulphuric acid made. In the great majority of cases sulphate-of-soda and superphosphate works make their own sulphuric acid, and, of course, do not concentrate it beyond their own requirements.

Touching the acid made for sale, however, a circumstance has to be considered here which in many cases induces the manufacturer to incur the great expense and trouble of concentrating the acid as highly as possible, even in cases where the consumer, not requiring it of such strength, must himself dilute before using it. This is the greater expense of packages and transit for the same weight of real acid in the dilute as

compared with the concentrated state. Apart from those cases in which completely concentrated acid is asked for on account of the smaller cost of packages and of transit, or from old habit and ignorance, there are many cases in which the consumer is really obliged to employ an acid of the highest possible strength:—for instance, the purification of rape-oil; that of benzol, paraffin, and other mineral oils; the refining of gold and silver; the production of nitro-cellulose, nitro-glycerine, nitro-benzene, and other nitro-compounds; that of sulphonic acids, for instance those of benzene and anthraquinone for the manufacture of resorcine and alizarine; for dissolving indigo, and many other purposes. In many cases an acid containing from 93 to 94 per cent. of  $\text{SO}_4\text{H}_2$  will do; and often that which is sold as acid of  $170^\circ \text{Tw.}$  does not contain more than that, and if pure, really ought to show only  $166^\circ \text{Tw.}$  ( $=1.83 \text{ sp. gr.}$ ).<sup>1</sup> For making nitro-compounds especially, however, an acid of greater strength is required, containing 97 or 98 per cent. of  $\text{SO}_4\text{H}_2$ ; even this cannot show more than  $1.840 \text{ sp. gr. at } 0^\circ$ , or  $168^\circ$  by a correct hydrometer, unless it is very impure and contains much foreign matters.

This "extra-concentrated" acid can also be made in platinum vessels, but at the cost of dissolving much more platinum than ordinary rectified oil of vitriol. In this way it is possible to get up to 98 per cent., or at most 98.5 per cent. These high strengths, as we shall see below, can also be made in cast-iron vessels, which are not suitable for concentrating acids below 96 per cent. For some purposes an acid of as nearly as possible 100 per cent., that is, monohydrated sulphuric acid, is required. This can be made by adding some fuming oil of vitriol to ordinary sulphuric acid; but it can also be made by freezing, as we shall see *infra*.

#### *Manufacture of Ordinary Rectified Oil of Vitriol.*

It has already been mentioned that usually either *glass* or *platinum* vessels are used for the last concentration of sulphuric acid. Which of these two materials is to be preferred to the other has been a matter in dispute for a long time; nor is it

<sup>1</sup> Recently more correct hydrometers have been used, and the quotations are no longer made for acid of  $170^\circ \text{Tw.}$  (which does not exist in the pure state), but  $168^\circ \text{Tw.}$

settled yet, both systems being largely employed. Formerly, before the platinum industry was developed, *glass retorts* were the only available apparatus, and those could only be had of comparatively small size and inferior quality. They were mostly set in "galley-furnaces," a double long row of retorts being heated by a fireplace at one end; thus the retorts near the fire were, of course, much more heated than those more distant, and were much sooner finished, or even overheated before the distant retorts had been sufficiently fired. Each retort was either put into a metal pot, with some sand between, or protected from the direct flame by a covering of clay and horse-dung. Both owing to the inferior quality of the retorts and the unsuitable setting, there was always much breakage, combined not only with the loss of acid, but also with the sudden evolution of suffocating vapours. The cracking of the retorts was, especially induced by a cold draught getting at them; and since in that case the workmen had to save themselves instantly from the vapours by leaving the room, frequently the cracking extended to all the retorts. Besides, the expenditure of time, wages, and fuel in this process was very great.

There was always, therefore, an inducement to discover some other material than glass for the last concentration of sulphuric acid; and the only practicable metal, *platinum*, was at once applied, in spite of its high price and difficult management, as soon as Wollaston's process of welding spongy platinum into ingots and plates was made known. The first platinum still appears to have been made in 1809 in London; it weighed 423 oz. (*Chem. News*, xxxviii. p. 43). Later on platinum stills weighing from 66 lb. to a cwt. were made, holding 4 to 6 tons of vitriol, and costing from £1600 to £2000. This large sum did not deter manufacturers from using platinum for the last concentration of sulphuric acid, because they convinced themselves at once of the large amount, facility, and safety of the work of concentration that could be carried on in them, and because they thought (although erroneously) they could reckon upon such apparatus lasting almost for ever.

The platinum vessels made by Wollaston's process were often porous and unsound, so that acid oozed through; besides, blisters and rents frequently appeared in them, which had to be soldered up with gold. The platinum stills themselves, there-

fore, gave much dissatisfaction. This, however, has been greatly diminished since Ste.-Claire Deville taught the melting of platinum in large masses by an oxygen gas blowpipe in furnaces made of quicklime, by which perfectly sound ingots of platinum weighing 2 cwt. are obtained; and, further, to solder the joints with platinum itself instead of gold, analogous to the burning of the lead chambers. In London this process was first applied in 1860. Since then the stills have been much more durable and at the same time cheaper, although the unavoidable concentration of the platinum industry in very few hands still tends to keep the price of platinum apparatus at a very high figure.

When, however, attention was drawn to the fact that platinum itself is gradually acted upon by sulphuric acid (see below), and that thus the large capital expended on the stills not only involves heavy permanent charges for interest, but has to be gradually written off altogether, and when, on the other hand, great improvements were effected in the manufacture and treatment of glass retorts, the latter came to the fore again, and began to drive platinum vessels out of the field, more especially in England. In 1862 Hofmann mentioned, in the *Report of the Jury*, that in Lancashire the use of platinum retorts had almost ceased; at that time about seven-tenths of all the vitriol in England was concentrated in glass. In France and Belgium glass retorts existed along with platinum stills; but the latter held a wider ground; and in Germany it was almost exclusively used. In 1868, the *Official Report of the International Jury*, vii. p. 34, stated that concentration in glass was then very rare (in France).

In order to meet the competition of glass, the platinum-works made efforts to construct the stills more durable and more cheaply; and they indeed recovered a portion of the field previously lost. Later on they were urged to renewed efforts in this line by the combination of platinum and lead employed by Faure and Kessler (p. 1142), which has again receded into the background; and eventually the introduction of gold-lined platinum has greatly advanced the use of these vessels.

At the present time the matter stands thus:—Both glass retorts and platinum stills are in use, some of the latter made according to the old and others according to the new system.

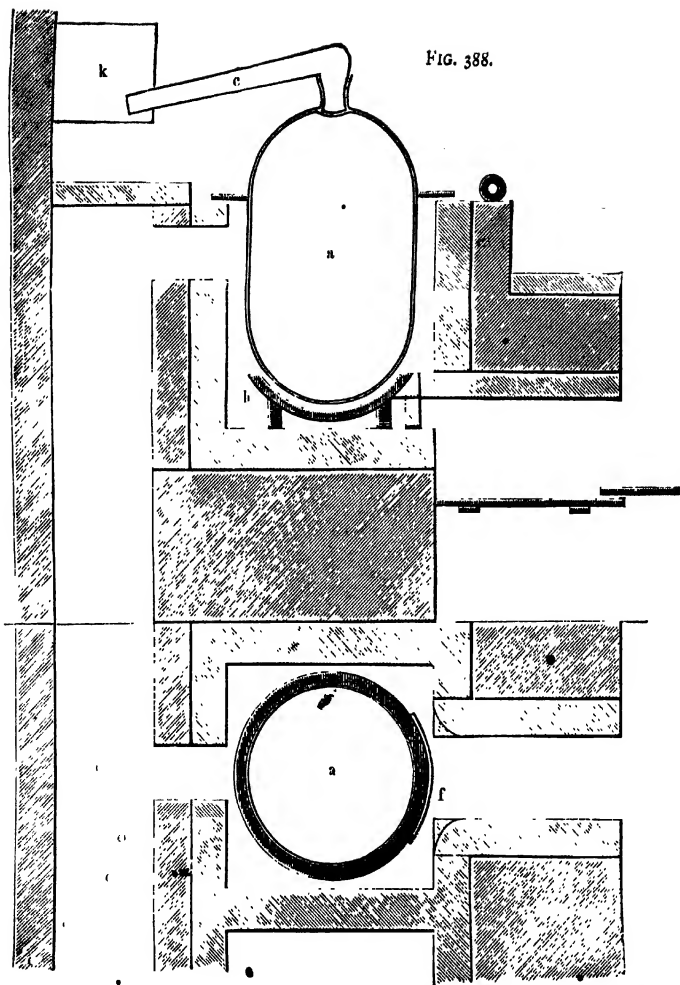


FIG. 388.

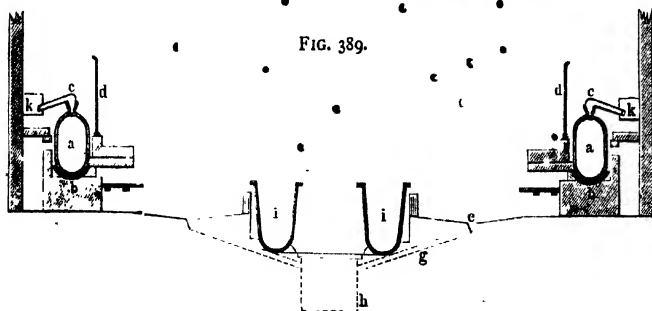


FIG. 389.

The glass retorts are mostly used for the less highly concentrated acid, containing 92 to 93 per cent., the platinum stills for the more concentrated acid, 93 to 96 per cent.; in a few cases both are employed at the same works for these different objects. The use of glass retorts, however, is almost entirely confined to England; on the Continent, platinum or platinum-gold vessels are used nearly everywhere but in a few places exceptionally well situated for obtaining glass retorts—for instance, Montpellier, where, according to Payen, a retort of 18 gallons capacity only costs 1.6 franc, whilst at Paris and most other industrial centres the price is 6 francs. Since such a retort holds a little over 1½ cwt. of strong acid, and on an average can be used five times, furnishing altogether 8 cwt. of vitriol, the retorts for 1 ton of acid at Montpellier cost 6 francs, at Paris, etc., 15 francs. In America both glass and platinum apparatus are used.

If the enormous rise in the value of platinum which has taken place since 1890 should prove to be permanent, the use of glass retorts, and also those of porcelain, cast iron, and the concentration by hot air, etc. (see below), will receive a fresh stimulus.

Lead pans have also been proposed for this purpose (*suprà*, p. 1086).

#### *Concentration in Glass Retorts.*

The shape of glass retorts now in use for concentrating oil of vitriol was introduced by Chance Brothers, of Oldbury, near Birmingham, who make them at their glass-works at Smethwick. They are shown in Fig. 388 (this, altogether with Figs. 389 and 390, is taken from Roscoe and Schorlemmer's *Chemistry*). These retorts consist of two separate parts, viz., a large bottle *a*, with a neck at the top, into which fits a loose head *c*, whose other end enters an aperture in a lead pipe or tunnel *k*, running all along the retort-house, and ultimately connected with a chimney. The bottles *a* are blown of thin glass, as evenly as possible, about 3 ft. high from the bottom to the top of the neck, and 1 ft. 9 in. diameter. They rest on a flat metal sand-bath *b*, and are protected from direct contact with the flame by the round fire-clay slab *f*. In the pipe *k*, which conveys the condensed acid vapours to a collecting-tank, there is always some suction produced by the chimney draught at the other end; therefore the head *c* needs no cement to connect it with the bottle, as no vapours can get out, only air being able to

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enter. This is very important, as the head *c* has to be taken off and put on every day. The above-mentioned suction has also this effect, that retorts may continue at work with cracks in their upper parts, provided such cracks do not reach down to the level of the acid in the bottle.

A number of retorts are always grouped together, as seen in Fig. 390, where AAA are boiling-down pans, from which the main pipe B takes away the hot acid of 144° Tw. On this pipe

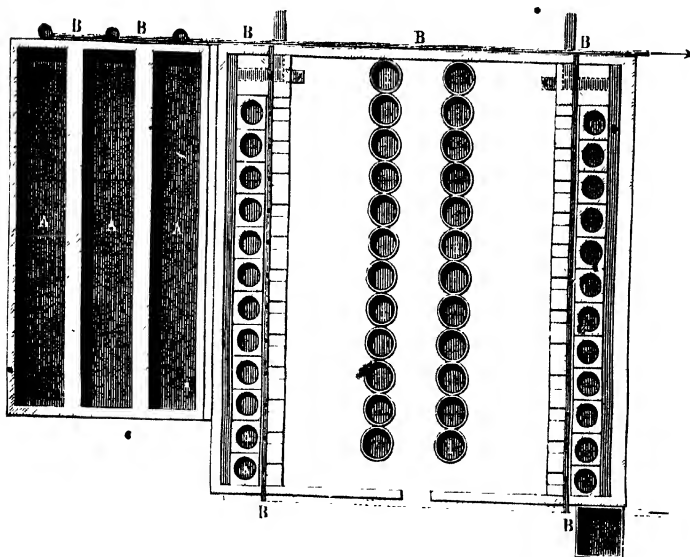


FIG. 390.

are fixed long thin lead pipes *d d* (Fig. 389), which are bent down at will, in order to fill the single retorts. *i i* are cooling-pots for the strong acid drawn off, from which the carbøys are filled. The floor is made a little sloping, so that in the case of a retort breaking the acid runs into the gutter *c*, and from this through pipe *g* into cistern *h*.

An accurate plan (to scale) of a retort-setting is given in Figs. 391 and 392; this will be intelligible without further explanation.

The retorts (in number from 20 to 50) are placed in a

separate house, the temperature of which is kept constantly at from  $25^{\circ}$  to  $30^{\circ}$  C., the building being provided with tight-

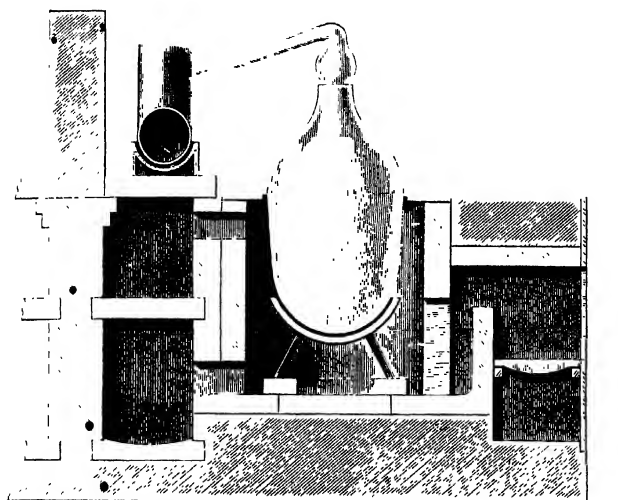


FIG. 391.

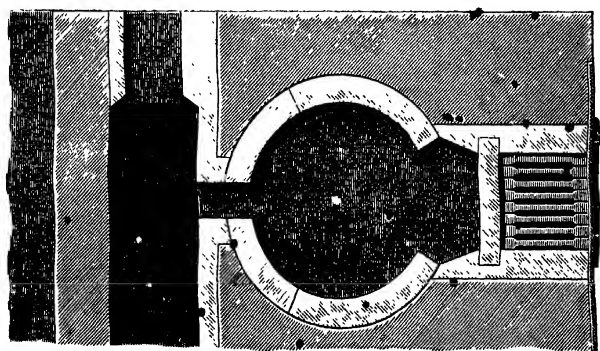


FIG. 392.

fitting windows and double doors; only one door is opened at a time, the other being shut, so that no draught (the chief



cause of the bottles cracking) can enter. A retort-house with twenty-four retorts can turn out about 5 tons per diem.

The work is carried on in this way:—The distillation goes on all day long, and is finished in the evening. During the night the acid cools down to some extent; in the morning the retort-heads are taken off and the acid is drawn off by siphons of platinum or thin lead tubing with a very narrow orifice. The siphon is filled with cold acid, the narrow opening closed with the finger; the siphon is then put in quickly, and the finger at once washed with water. Sometimes the acid is thus drawn directly into glass carboys, but it is better to employ a series of cooling pots, as shown in Figs. 389 and 390. A small portion of the acid is necessarily left in the retorts, and this is useful in refilling them with warm acid of  $144^{\circ}$  Tw., as it prevents cracking.

In order to prevent the cracking of the retorts by sudden draughts, Jones patented, in 1845, so-called "protectors," consisting of hoods of sheet-iron or stoneware, made in two parts, quite covering the neck of the retort. But as this also prevents observation of the liquid, they are inconvenient; and they are quite unnecessary if the house is arranged as described above—that is to say, if it is kept warm, and draughts are excluded by double doors.

The sulphuric-acid *vapours* formed in the rectifying process in glass retorts should in no case be allowed to get into the chimney. They are partly condensed in the conducting-pipe itself; after issuing from this, they should pass through a small coke condenser, flushed with water, before entering the chimney, to wash out all the acid. The *21st Alkali Report*, p. 45, describes the following arrangement:—The necks of the retorts pass into a lead trunk, set on a level, whose bottom is dished with an upstand of 3 in., not burnt to the sides. A small stream of water is set running, when the glasses start boiling, at the end of the trunk nearest the condenser, and the water travels in a contrary direction to the vapours; at the further end it runs out at a lip as acid of  $100^{\circ}$  Tw. This plan is very effective, and only a small scrubber is required to arrest all the fog of acid vapour escaping from the trunk.

Fehrmann (*Fischer's Jahresber.*, 1886, p. 263) describes the glass concentrating-plant at Mulheim on the Rhine. The

retorts had a similar shape to those used in England; they were made at Glasgow and cost at Mülheim about 38s. each. The construction and working of the plant at the Mülheim works have been very minutely described by Lütj (Z. angew. Chem., 1892, p. 385). This communication would be very important and interesting if the intermittent plan were not now universally recognised as far too expensive, and therefore antiquated; I must therefore refer those still interested in it to the original or to the translation in *J. Soc. Chem. Ind.*, 1893, p. 153. The plant described by Lütj (erected by an English chemist) seems to have been less economical than some others and is a warning example against the whole system.

In England formerly all sulphuric-acid retorts were made of flint glass, containing upwards of 40 per cent. lead oxide, because this was supposed to stand better, which may possibly have been caused merely by the fact that the retorts were not made to do so much work as in recent times. On the Continent such retorts have been always made of ordinary soda-lime glass (crown glass), and this seems to be used in England as well now.

A great improvement on the old plan of intermittent concentration in glass retorts is the *continuously acting plan* of Gridley, patented as a communication by Mr Henry Chance (B. P. 1243 of 1871). Several retorts are placed terrace-wise in an obliquely ascending furnace and are connected by siphons, so that the top retort is fed by fresh acid, which, after being concentrated to some extent, flows into the next lower retort, and so on. The lowest retort is placed in the hottest part of the furnace. A retort is shown in detail in Fig. 393.

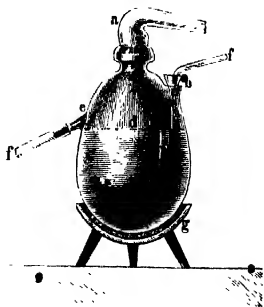


FIG. 393.

*a* is the head, connected with a draught-pipe common to all the retorts, by which the vapours are conveyed into a small leaden coke-tower and condensed by water. At *b* there is an opening in the shoulder of the retort; into this the funnel passes by which the acid enters the retort; *d* shows the level of the acid; *e* is the

tubule attached to the retort, by which the acid leaves it; and *ff* show the glass connectors which convey the acid from one retort to another. The retorts are set in sand in shallow iron pots, *g*. Four beds of retorts, *i.e.* sixteen retorts, will produce, from 6 A.M. on Monday till 12 noon Saturday, 600 carboys, equal to 46 tons; they are worked by two retort-men (day and night turns) and two labourers. The average consumption of coal is 28 lb. per carboy of 175 lb. (=16 per cent.). This process is in very successful operation in several vitriol-works in the United States, and has also been adopted by some manufacturers in England.

I owe some important communications concerning improvements in the Gridley process to the kindness of Messrs Chance Brothers, of the Oldbury chemical works, and of their manager, Mr H. C. D. France. (Part of the following is taken from Dr Ballard's *Report*, pp. 173 and 182). The process has been improved at the above-mentioned works by using ordinary coal-gas as a heating agent, burnt in a Bunsen burner underneath each retort. This has largely increased the output and decreased the labour and breakage. The breakage during a period of two years has only cost 3d. per ton of acid rectified, and the labour has been 1s. 10d. per ton; but this item could easily be lessened, as the same men could look after plant turning out twice as much. The gas consumed (made at the works themselves), with all leakages and defects, amounts to 3500 cub. ft. per ton of acid of sp. gr. 1.84. (The present consumption of gas is probably even less than that here stated.)

Figs. 394 to 396 show the way in which the four retorts are combined in a set, which is fired from a common gas-pipe.

The retorts are first fired till all the acid in each of them has attained full strength; then fresh acid of 144° Tw. is run into the top retort, whereupon the connecting overflow-pipes begin to work and the acid runs from each retort into the next lower one, and from the lowest into a cooler, from which it can be filled into carboys. This process goes on day and night.

A great advantage of the Gridley-Chance plan is this, that it requires no retort-house kept at the temperature of a Turkish bath, like the old plan. It is only necessary to enclose the four retorts themselves in a glass case, similar to the vapour hoods to be found in every large chemical laboratory, in order to

protect the retorts against draughts. The glass case is connected by a pipe with a small leaden coke-tower, which communicates with the chimney; any acid vapours escaping from the retorts are condensed here.

The Gridley plant, as arranged at Chance Brothers, is so efficient that with ordinary care breakages of retorts hardly ever occur. But in order to provide against this contingency, the bottom of each fireplace communicates by a pipe with an underground tank; in case of a retort breaking the acid would flow into this tank.

The strength of acid attainable by this (or any similar continuous) process does not exceed 92, or at most 93 per cent., which must not be overlooked in comparing the cost of concentration with different kinds of apparatus.

The cooling of the concentrated acid in this process is carried out in such a manner that the hot acid first flows through a platinum tube, in which it already loses a good deal of its heat, and then into a leaden box with double walls and external and internal water-cooling. The acid issues perfectly limpid, about 60° C. warm and 168° Tw. strong. (Of course any of the cooling-apparatus connected with platinum stills, as described further on, might be employed here.)

Bowen (B. P. 2035 of 1883) describes an apparatus in which the vapours from each lower retort pass into the next higher one, so that very little sulphuric-acid vapour leaves the last retort. [Rational as this seems at the first glance, it is still very doubtful whether in this way the concentration will not be interfered with too much.]

Veitch (B. P. 7901 of 1889) employs flat-bottomed retorts, arranged one above another on a stepped terrace within a tapering fire-flue common to them all, the fire being placed at the lowest and widest end, and the flue narrowing upwards. The acid enters in a constant stream, travelling through the whole series. All the retorts are easily visible.

Penniman (Amer. P. 469439) employs in a set of retorts arranged stepwise a current of air, which keeps the acid continually agitated, and so prevents their breaking.

Retorts having the lower half composed of glass and the hood of any suitable material are described by Schofield (B. P. 19780 of 1891).

# 1118 THE CONCENTRATION OF SULPHURIC ACID

*Costs.*—The cost of concentrating in glass requires much more labour than platinum stills, and this is also of a disagreeable kind. The consumption of fuel is sometimes absurdly stated to amount to eight times the consumption with platinum stills; in direct contrast is the following statement by P. W. Hofmann, referring to the cost of concentration at Dienze, where  $2\frac{1}{2}$  tons of concentrated acid were daily made in glass retorts, viz., for 1 ton:—

	s.	d.
4 cwt. of coals . . . . .	4	0
Wages . . . . .	3	0
Breakage of carboys . . . . .	1	0
	8	0

If the precaution is taken of replacing all the carboys by new ones after the lapse of six weeks, whether they seem damaged or not, there is next to no breakage, and the cost of concentration is reduced to 7s. 6d. per ton (*Hofmann's Official Report*, 1875, vol. i. p. 188). With this should be compared the very much higher cost for wear and tear of the platinum stills (to be given below), and, on the other hand, the much higher statement by Payen concerning the breakage, which, however, refers to the imperfect retorts of former times. Payen states that at Tennant's works at Glasgow the breakage, on an average, was only seven retorts per annum. These retorts were made (by Perceval, Vickers, & Co., of Manchester) from green soda-glass, as even in thickness as possible, blown with special care, and cooled very slowly; their weight is about 60 lb. each, and they cost 1s. 4d. per lb.

Another statement concerning the cost of concentrating in glass retorts is made in the *Mineral Resources of the United States*, for 1886, p. 673, as emanating from a large English works where acid of 60° Bé. coming from the Glover tower [?], is concentrated to 66° Bé. (8 tons per day):—

	£	s.	d.
1 ton of coal . . . . .	0	16	0
Wages and superintendence . . . . .	2	0	0
Breakage of retorts . . . . .	0	8	0
Wear and tear of other materials and interest on plant (estimated to cost £200, at 50 per cent. per annum) . . . . .	0	6	0
Cost of concentrating 8 tons . . . . .	3	10	0
Cost of concentrating 1 ton . . . . .		8	9

[This estimate is evidently utterly unreliable. The amount of coal is absurdly low, the breakage of retorts excessively high. We refrain from quoting the comparative cost of concentration in a Faure and Kessler still given in the same place, as equally misleading.]

The cost of concentrating in a Gridley's apparatus (p. 1115) is, of course, considerably lower than in ordinary retorts, as there is less consumption of fuel, less labour, and next to no breakage of retorts.

According to a very interesting comparative survey by Tate (*J. Soc. Chem. Ind.*, 1894, p. 208), to which we shall have again to refer, the cost of a set of glass retorts on the old system, for making 10 tons in twenty-four hours, ranges from £800 to £1000, inclusive of condensing-apparatus. The cost of concentrating from sp. gr. 1.76 to 1.838 varies very much; but the consumption of fuel averages 13 to 14 cwt., and the wages 4s. 6d. per ton of strong acid. The breakage varies extremely at different places. With the Gridley-Chance system the cost of two sets of four retorts each, for making 23 to 25 tons acid per week, is £200, and £100 for the building. The cost of labour is only from 2s. and 3s. per ton of strong acid; of coal only two-thirds of the quantity required by the old system is necessary, say 10 to 12 cwt. per ton. [This does not agree with the above statement, and later on only 5 cwt. is spoken of.] The breakage is only about one retort to 180 or 200 tons of acid, or say, 1s. per ton (a retort costs 25s.; in discussing the paper it was mentioned that the breakage is frequently much higher). Extra-concentrated acid is more easily made in glass than in platinum retorts. Acid contaminated by suspended or dissolved impurities is not easily concentrated by this system, as it causes much breakage.

In the *Chem. Trade J.*, 1906, xxxviii. p. 77, the cost of glass-retorts for rectifying sulphuric acid is stated at £23 per glass, which includes all pans, coolers, etc. Each glass will turn out 1 ton per week of sp. gr. 1.840, but an excess of glasses must be allowed for breakages. Thirty glasses usually turn out 27 tons per week, and consume  $4\frac{1}{2}$  cwt. of coal per ton of R.O.V.

*Concentration in Porcelain Dishes or Bakers (Cascades).*

Hughes, in Amer. P. 339552, describes an apparatus consisting of porcelain dishes with glass heads, otherwise similar to the glass-retort apparatus of Gridley-Chance (*suprà*, p. 1115). The use of porcelain dishes was also patented in the United States by W. H. Adams, in 1887 (Scheurer-Kestner, *Bull. Soc. Ind. Mulhouse*, 1892, p. 317).

Messieurs Ch. Négrier et Cie., at Périgucux, have constructed a furnace for evaporating sulphuric acid from  $50^{\circ}$  to  $65\frac{1}{2}^{\circ}$  Bé. (say, from  $106^{\circ}$  to  $167^{\circ}$  Tw.) in porcelain capsules (B. P. 14022 of 1890). Their apparatus is shown in Fig. 292, facing page 693 of our second edition. (It is omitted here as being superseded by Benker's pans, to be shown later on.) It consists of two parallel ranges of eight porcelain capsules, each placed one above the other, so that the acid overflowing from the lip of each upper pan flows into the lower one. The capsules are semi-circular, 0.305 m. wide and 0.135 m. deep. Every two dishes placed on the same level are contained in suitable pans, forming cavities of a single cast-iron plate, reaching from one side of the furnace to the other. Asbestos tissue is interposed between the capsules and the metal-pans, in order to protect the capsules and prevent bumping, which is further lessened by putting fragments of porcelain inside the capsules. In the case of a capsule breaking (which happens but rarely) its contents can escape into the fireplace through several holes left in the metal pans; when this is perceived, the feed of acid is stopped, the cover is lifted, and the broken dish is replaced by a fresh one in ten minutes. An iron plate with its two dishes lasts three or four years. They are shaped in such a manner that there is no communication between the space below, destined for the fire-gases, and the space above, where the acid vapours are formed, the joints being made good with a cement of asbestos and silicate of soda. When the capsules have been placed in the pans, a layer of coarse sand is put into the space between them up to the edge of the capsules. Every pan has two shoulders, destined to prevent the dilatation caused by heat from bringing it into contact with the next higher capsule. The brickwork above the level of the capsules is made of silica bricks; the top cover is made of cast-iron or glass. The acid

gases are aspirated<sup>d</sup> by a jet of water, or in other suitable manner, and are condensed or not. The heat of the fire-gases issuing from the apparatus is used for bringing up acid from 50° to 60° Bé. in a similar apparatus or in lead pans.

One such apparatus is stated by the inventor to produce 18 to 20 cwt. concentrated O.V. from acid of 60° Bé. (142° Tw.), with an expenditure of about 13 per cent. of coals of somewhat inferior quality. According to further information received from the inventors, they bring their acid from 53° to 65°·5 Bé. with 21 per cent. of the same coal.

This system is minutely described by Kretzschmar in *Chem. Zeit.*, 1892, p. 418. The gases from a set of four furnaces pass underneath three sets of lead pans, where they concentrate the acid up to 134° to 142° Tw., and heat it to 145° or 149° C. Every furnace produces 25 cwt. of acid of 93 per cent. daily, with an expenditure of 23·5 per cent. of rather low-grade English coal. The breakage of dishes per month was at first 5, out of a total of 64, costing 4s. each; but this was greatly lessened when the cast-iron bed-plates were replaced by fire-clay slabs. The acid vapours from every set of two furnaces pass into a lead condenser, then into a cooling-worm, and eventually into an upright pipe, in which the necessary draught is produced by a jet of compressed air. The Négrier apparatus has the advantage of allowing the use of impure and nitrous acid, but it requires much more space, labour, and coal than platinum stills. This apparatus had been erected at the Rhenania works, Stolberg, but was given up as causing too much expense for fuel and breakage of dishes, and performing too little work. •

Lemaitre's Fr. P. 357555 contains several improvements of the Négrier furnace.

F. Benker has erected in France a number of apparatus concentrating sulphuric acid in porcelain dishes, covered with a special protecting cement and heated by several small fires. The whole is enclosed in a chamber built of Volvic lava, and the capsules very rarely break. The acid thereby obtained is stated to be much purer than that made in platinum, and perfectly clear. It can be brought up to 97 or 98 or even 99 per cent., and then deposits all iron salts; at a French factory such acid (made from Sain-Bel pyrites) is diluted with distilled water and sold for use in storage-batteries. Benker's system



as formerly constructed, is shown in Figs. 397 and 398; but according to a paper by Hartmann and Benker, in *Z. angew. Chem.*, 1906, p. 564, they now build the apparatus somewhat differently, and this new plan will be described below. The dishes are all placed on fire-clay rests and are cemented in these with asbestos and water-glass, so that the fire-gases are altogether separated from the acid fumes. They are cleaned out once every six or eight weeks, and exchanged after six or eight months. By special precautions in manufacturing, they are now made practically unbreakable, but in case of an accident they can be exchanged with a stoppage of only two or three hours. The acid fumes are condensed in lead-lined boxes filled with bits of stoneware of the size of a pea.

The heating now takes place, not by means of four small fireplaces, as shown here, but by a single large fireplace (800 × 380 mm. grate surface), so that, in lieu of coke, coal can be used for firing. There are now 24 dishes in each cascade, or 48 in both; the four lowest dishes of each row are protected by a curtain arch, so that the acid therein boils quietly without spurting. The porcelain dishes are placed in fire-clay dishes, with a layer of dry asbestos between them, which affords such a good protection that on an average there is only one dish cracked every five or six months. Very little of the acid distils over, and this is only 4° to 8° B $\acute{e}$ . strong, which is a very economical result. The present apparatus, with 48 dishes, furnishes per annum 2100 to 2300 tons acid of 92 to 93 per cent.; or 1500 to 1600 tons of 95 to 97 per cent.; or 1200 to 1300 tons of 97 to 98 per cent.; or 1000 to 1100 tons of 98 to 99 per cent. In Germany the cost of such an apparatus in 1906 was from £550 to £600, inclusive of condensing and cooling arrangements. The consumption of coals, starting from chamber-acid of 53° B $\acute{e}$ ., is 15 to 17 per cent. for acid of 95 to 97 per cent.; or 24 per cent. for acid of 97 to 98 per cent.; or 27 to 30 per cent. for acid of 98 to 99 per cent.; this is claimed to be much less than the consumption in Kessler's apparatus (p. 1142). In 1906 64 Benker plants were actually at work (21 in France, 11 in Germany, 11 in Austria, 7 in Spain, 4 in Sweden, 4 in Russia), and a number of others were to be started soon, one of them in England.

As we shall see later on, the great success of the plan just

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*Beaker-apparatus.*

This kind of concentrating-apparatus was first introduced by Webb, followed by Levinstein and others. Their principle is quite similar to the dish-apparatus. The material used is either glass or porcelain.

Webb's B. Ps. are Nos. 2343, 17407, and 18891, all of 1891. As Figs. 399 and 400 (p. 1125) show, his apparatus consists of 14 or 16 glass or porcelain beakers, A, A, arranged one above the other, about 11 in. wide and 21 in. high, with overflow lips communicating with movable tapering glass pipes, placed in a slanting position in the next lower beaker, so that the acid flows from each beaker on to the bottom of the next, and from the last of these through a cooler into the vessels where it is to be stored. According to Webb's B. P. 2343 of 1891, a series of glass vessels are placed on slabs, arranged in steps, in a heating-chamber; the vessels are enclosed near their upper edges in iron plates or slabs, corresponding to the bottom. In every one of these vessels is placed at an angle a loose tapered glass tube, reaching from the spout of one vessel to the bottom of the next lower vessel, where it is provided on its side with an outlet-slit. The fire-gases pass first into combustion-chambers on one side of the heating-chamber, and from thence into the space left round the glass vessels. The weak liquor is fed into the tube of the uppermost vessel and displaces a certain amount of acid, which will overflow into the tube of the next vessel, etc., thus causing a thorough interchange in the liquor to be evaporated. The concentrated acid is delivered from the last vessel of the series.

Much stress is laid on the fact that the acid always flows on to the bottom of the next lower beaker, where it forces the already concentrated acid upwards and is well mixed with it.

According to the inventor, the cost of an apparatus of 14 glasses, apart from patent royalty, is from £60 to £100. Usually two sets are built together. Fourteen glasses produce per hour a carboy of acid of sp. gr. 1.838 from acid of 1.74, with consumption of less than  $\frac{1}{2}$  cwt. of coke. One man can attend to four sets of 14 glasses each, in which case the cost of labour is only 2d. per carboy. Every set makes 5 or 6 tons of strong acid per week from acid of sp. gr. 1.60, or 11 to 12 tons from acid of 1.74.

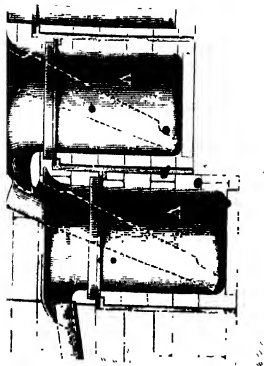
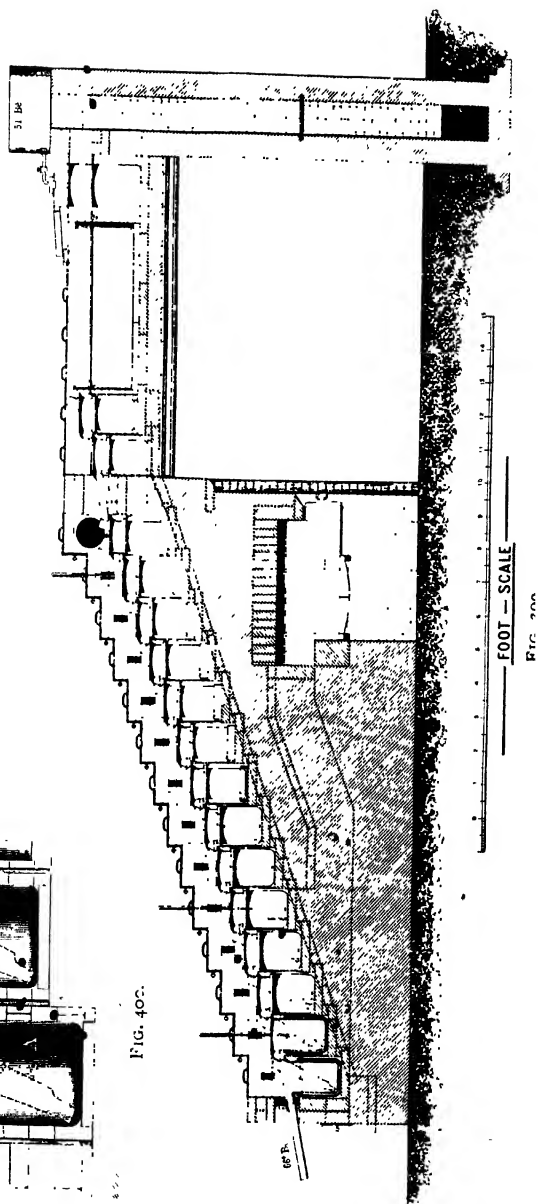


FIG. 400.



According to actual observation, at first the breakage was very considerable, in fact intolerable, so long as all beakers were made of glass. Therefore the three bottom beakers of every set were replaced by porcelain vessels, by which the breakage was greatly reduced. More recently *all* the beakers have been made of porcelain or of stoneware, and since then the breakage has been very slight. The feed of acid is regulated by means of a thermometer placed in the fourth beaker from the bottom. No lead pans are needed for preliminary concentration. Even the most impure acid, also waste acid from dynamite-works, etc., can be worked up. The acid running off in cases of breakage is easily caught and used over again.

A fresh patent of Webb's (B. P. 29884 of 1896) describes a firing arrangement by a gas-producer, where the flame does not act from the higher end down to the lower, but *vice versa*.

The illustrations of Webb's apparatus, published in certain periodicals during 1901, differ from those given here only in two respects: first, the fireplace is not below the top beakers, but about midway; second, a number of upright pipes take the acid fumes away into a main pipe and lead them into a condenser, where the acid is to be kept back from escaping into the atmosphere.

Webb (B. P. 1515 of 1901) also describes an apparatus for retaining the acid fumes, consisting of a wooden box, lined with lead, closed at top, with a funnel-pipe reaching nearly to the bottom for admitting cooling-water, which overflows near the top. The tank contains two metal boxes, connected by a number of pipes, the first of them fitted with several water-tubes. The acid fumes enter at the top of the first box, pass through the connecting-pipes into the second box, and issue from the top of this into a chimney, which produces the necessary suction. On their way the fumes are cooled by the water surrounding the boxes and flowing through the water-tubes and are thus condensed; the liquid thus formed runs off at the bottom. In order to retain the acid longer in the first box, the pipes connecting it with the second box are furnished with nozzles which throttle the orifice.

A further patent of Webb's (B. P. 1516 of 1901) describes beakers consisting of an outer vessel and an inner vertical vessel, the latter having at its lower end lateral openings, and its top reaching above the outlet bib of the outer vessel, for the

purpose of dividing the liquids into two columns. There is also a removable spout attached to the top of the beaker.

This modification appears to be that which is mentioned in the 38th *Alkali Inspectors' Report*, and described in the Ger. P. 135886, by F. G. Webb and Webb's Patents Limited. There is a stepped series of beakers, each of them containing an inner cylindrical vessel, not much narrower than the beaker itself, open at the top, and communicating by holes at the bottom with the annular space between the two vessels. The acid overflows by a lip from each of the outer beakers into the inner vessel of the next lower beaker, passes through the bottom holes into the annular outer space, and overflows from this into the inner vessel below. The whole may be placed in a hot-air oven. Or else the top edges are formed in such a manner that a still-head may be placed on each beaker, with an arm connected with a slanting draught-pipe [cf. Gridley's apparatus, p. 1115], from which the vapours are taken into a tubular water-condenser before passing into the draughting-shaft: in this case the beakers are heated only in their lower part.

Levinstein's patents are: 19213 of 1892; 2476 and 2835 of 1893; 22844 of 1894; his apparatus is very similar to Webb's, but the beakers have rounded bottoms and are placed in metal dishes, and the overflow-pipes are modified. According to one of his latest patents, the dilute vapours from the upper portion and the strong vapours from the lower portion of the battery are carried away separately, which appears to be a very rational process.

Quite similar to the above is Bradbury's apparatus, B. P. 22327 of 1893; J. W. Scott's B. P. 14215 of 1894; R. Wilson's B. P. 14221 of 1895; and Schwab's B. P. 22512 of 1896.

Viaillieux and Perrin (B. P. 28302 of 1909; Fr. P. 397080) facilitate the condensation of the vapours, arising in the concentration of sulphuric acid, by embedding in the coke used for this purpose serpentine in which cold water or acid circulates, or by moistening the coke.

H. E. Green (B. P. 27209 of 1911), in order to economise space, makes the cascade double back upon itself.

Mackenzie (B. P. 6415 of 1909) provides for the dishes of cascade apparatus air-pipes for the purpose of agitating the contents of each dish, so that the impurities do not settle on the bottom and cause overheating.

Many cascade apparatus, especially on Webb's plan, have been erected in England, but some of them seem to have been discontinued, partly on account of excessive breakage of the glasses (which does not seem to happen so much with porcelain beakers), partly because they consumed too much fuel, and partly because it was found impossible to prevent the escape of dense white fumes from the chimneys (which were themselves sometimes ruined by these fumes and had to be rebuilt). The *Alkali Reports* of several years teem with complaints of this sort. The reason seems to be the same as that quoted in the case of the lead pans with surface-evaporation, viz., the formation of an acid mist of tiny, liquid, vesicular drops (p. 1081), or else the difficulty of condensing sulphuric anhydride (Chapter XI).

A. Nobel proceeds on the following principle (Ger. P. 10149 of 1880):—Since cast-iron is not acted upon by the vapour of sulphuric acid, the concentrating-apparatus is made in the shape of a column consisting of cast-iron pipes, in which porcelain dishes are placed on ledges. Each dish has an opening, through which a glass rod reaches into the next lower dish; this is intended to prevent the acid from splashing about in its downflow from dish to dish. When all the dishes are filled, the column is heated by flues surrounding it on the outside. The acid vapour, as well as the concentrated vitriol, is taken away at the bottom. Even nitrous vitriol is said to be used in such towers.

Another kind of column combined with the system of stepped beakers is the apparatus patented by Guttman (B. P. 16220 of 1898). It arranges glass or porcelain beakers, with overflows, in a vertical spiral column. They are placed on iron dishes, attached to curved, hinged doors, which together form a vertical heating-column, within which fire-gases surround the concentrating-beakers. Another patent (Ger. P. 109247) of his describes an arrangement for heating up the air required for the combustion by means of the waste heat of the apparatus.

A Guttman concentrating-tower has been erected in England, but it is fired by coke instead of gaseous fuel, and has been otherwise modified with a view to reduce breakages (*Alkali Inspectors' Report*, No. 38, p. 128).

According to Pohl (*Z. angew. Chem.*, 1912, p. 1851) the "vitreosil" (fused quartz, *suprà*, p. 1123), as manufactured by the

Deutsche Ton- und Steingewerke at Charlottenburg, in lieu of porcelain, gives excellent results. The Alkali Inspectors' Report for 1911 (*J. Soc. Chem. Ind.*, 1912, p. 716) also recommends the use of fused quartz or of "tantiron" for cascade apparatus.

The Adamson Chemical Company (Ger. P. 104679) concentrate sulphuric acid in two horizontal stoneware cylinders; a number of vertical stoneware or glass pipes, closed at the bottom, are suspended from these cylinders in a vertical position, reaching downwards into the fireplace and increasing the heating surface. [This is the system of "Field tubes" applied by de Hemptinne in his apparatus described in our first edition, Vol. I. pp. 507 *et seq.*, which has never been carried out in practice.]

Brandenberg (Ger. P. 243544) employs an evaporating-vessel with one or more inclined side-tubes, placed in a furnace. These side-tubes are provided with siphon-tubes inside the evaporating-vessel, which produce a vivid circulation of the liquid. If they are heated, the liquid inside the vessel is gradually heated up as well, and is brought to boiling. The mud settles at the bottom without interfering with the boiling-operation. This apparatus may be made of quartz, glass, or the like, as each part of it can expand without any strain being put on the other parts.

#### *Concentration in Platinum Stills.*

The arrangement of platinum stills formerly employed is very fully described and illustrated in the first edition of this work, pp. 526 to 530, and in our second edition, pp. 695 *et seq.* A number of data referring to the sizes, cost, and producing-power of those older stills is also there given; but all this must be considered antiquated, and we shall here describe only the modern shapes of platinum stills.

Since so much competition was made with the platinum stills, first by the improved glass retorts, and afterwards by the combined platinum-lead apparatus of Faure and Kessler, the two manufacturers of large platinum apparatus (Desmoutis, Lebrun & Company, of Paris, and Johnson, Matthey & Company, of London) both greatly improved the construction of platinum stills. In the first place they made them lighter, by leaving the greatest strength entirely in the bottom, directly



exposed to the fire. Already in 1867, Johnson, Matthey & Company had exhibited at Paris an apparatus for 5 tons per diem, costing only £1640, and another for 8 tons per diem at £2500.

Later on they recommended a lighter shape of still, intended for continuous work. A double still of that kind, for producing  $4\frac{1}{2}$  or 5 tons concentrated acid per day, cost £1200, a triple still, for  $7\frac{1}{2}$  or 8 tons acid, £1750. At that time stills with their special cooling-apparatus found much favour, but they are equally out of date now.

The modern platinum stills are mostly on the system of Prentice or of Delplace, as shown here.

Prentice's system (Figs. 401 to 403) contains, in the place of the former circular stills, a still of elongated square shape, say 3 ft.  $\times$  1 ft. 6 in. for 4 or 5 tons O.V. per day. The acid enters at the back end and runs out in front by an overflow. A still of this kind weighs about  $\frac{1}{2}$  cwt., and costs (formerly) about £1000, inclusive of overflow, cooler, metal ring, etc. The firm also supply platinum pans with corrugated bottoms, as shown in Fig. 401; but ordinary lead pans may be used instead.

Special statements concerning these stills, as introduced at the Griesheim works, will be found in *Chem. Ind.*, 1878, p. 194, and 1879, p. 109.

The favourable effect produced by Prentice's plan is principally owing to the corrugated bottom of the pans, which increases the heating-surface in the proportion of 1.57 to 1. The thin stratum of acid is a feature common to all more recent plans.

Another system, manufactured by Messrs Johnson, Matthey & Company, and introduced at some of the largest works, is that of Gustave Delplace, of Namur, which is shown in Figs. 404 to 406. In this apparatus two stills, A and B, are combined. The top still A is fed with acid of 144° Tw. and the distillate from the still B. The latter, also of platinum, carries on the concentration to the highest attainable point, even up to 98 per cent.  $\text{H}_2\text{SO}_4$ , if needed.

C C are heads and arms with outlet at E for the strong distillate; the weaker not condensed vapour goes away at E. F is a bottle-shaped cooler for receiving the concentrated acid from the stills. G is a lip attached to the first still for receiving the acid from the lead pans and the distillate from B B. H is a tube for receiving the condensed distillate and carrying it

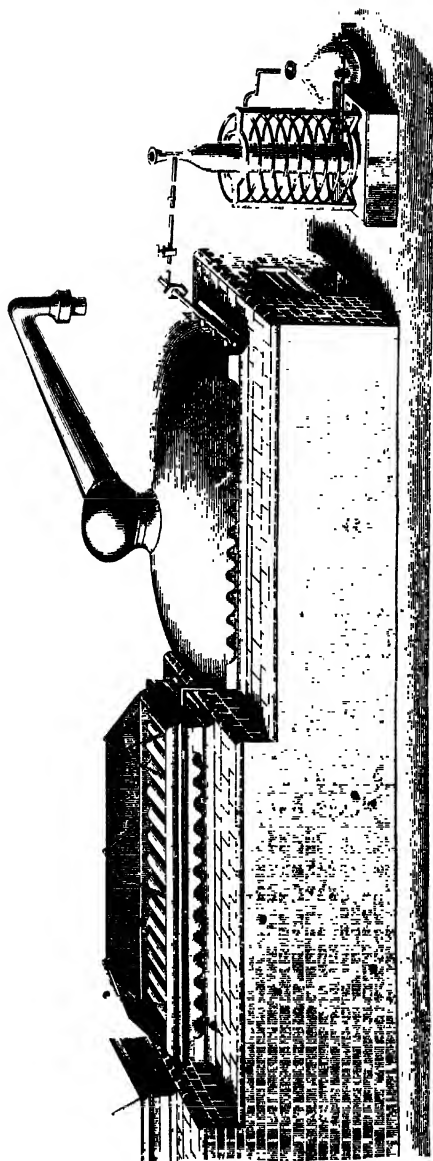


FIG. 401.

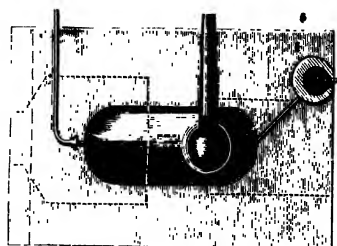


FIG. 402.

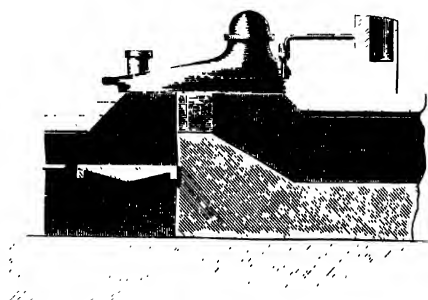


FIG. 403.

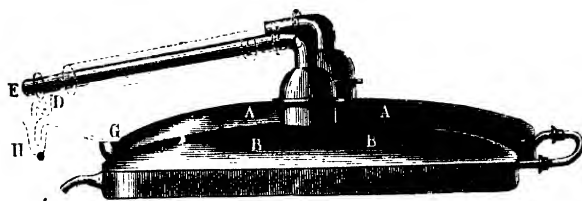


FIG. 404.

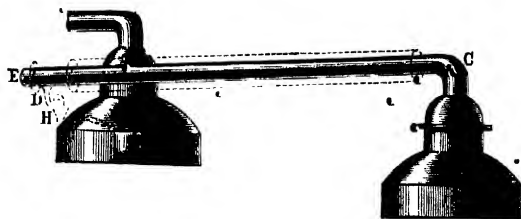


FIG. 405.

back to A A. In this apparatus the acid may be brought to 79 or 80 per cent.  $\text{SO}_3$ , or 97 to 98  $\text{H}_2\text{SO}_4$ . If this stronger acid, indispensable in the manufacture of dynamite, etc., is made, the distillate must be allowed to get up to  $150^\circ$  or  $155^\circ$  Tw., and is always conveyed back to the first still. For making the ordinary O.V., testing  $168^\circ$  Tw., which really contains only 73 to

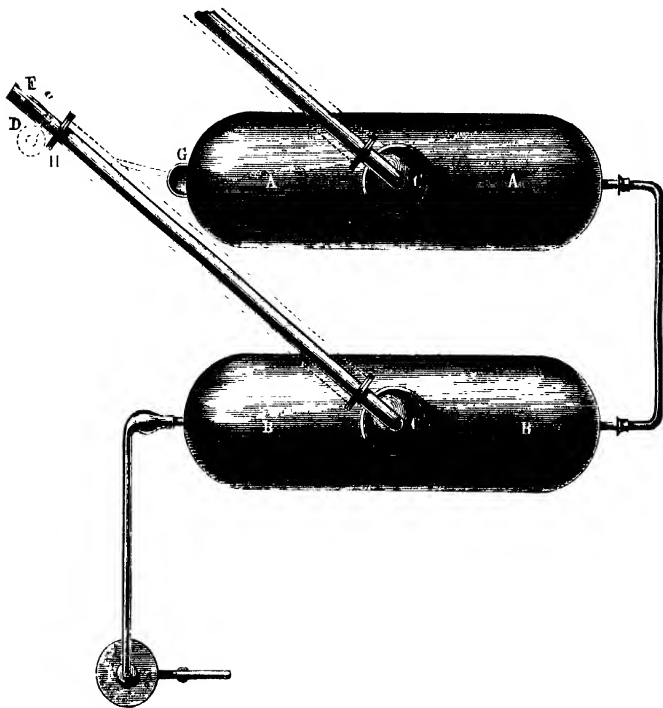


FIG. 40b.

76 per cent.  $\text{SO}_3$ , the distillate should show only  $7^\circ$  to  $23^\circ$  Tw., according to the speed of work, the feed-acid being  $144^\circ$  Tw. strong. The following advantage is claimed for the rectangular shape of still—that, in working for the most highly concentrated acid, the ferric sulphate cannot collect in the opening of the discharging-pipe, which generally happens with the ordinary apparatus; the distillate is also said to be weaker, the output

larger, in proportion to the evaporating surface, and the consumption of coal smaller than with the round shape. Instead of lead coolers, the distillate is condensed by a platinum tube  $2\frac{1}{4}$  in. wide, which is cooled by water for a length of 5 ft.; together with the head it weighs no more than the former large head and arm for connection with a lead cooler, without being liable to the frequent need of repairs of the latter; it also permits condensing acid of any strength, free from lead. Consequently the concentration may be carried to any required extent, whilst with lead condensers, and still more with Faure and Kessler's system, the great wear and tear of the lead do not permit this.

For making the very strongest acid by a continuous process (which previously was quite impossible), two long stills are preferable to one, the distillate from the second still running back into the first quite hot, without contact with lead; only the first weak distillate escapes.

The cooling of the concentrated acid is done by an upright platinum cylinder standing in water. The acid enters at the top and leaves it at the bottom; the water enters the outer vessel at the bottom and leaves it near the top.

The apparatus is supplied by Messrs Johnson, Matthey & Company by weight, at market prices for platinum. The weight of one boiler is about 50 lb.; head, condenser, and acid-cooler together  $17\frac{1}{2}$  lb. With this 5 tons of acid of 93 to 94 per cent. monohydrate, or 6 tons of 92 per cent. monohydrate (the common "168° Tw."), are made. A two-boiler apparatus, weighing about 110 lb. with all appurtenances, furnishes 10 tons of O.V. at 93 to 94 per cent., or 12 tons at 92 per cent., in twenty-four hours. M. Delplace (Ste. Croix 7, Namur) undertakes the erection and starting of the apparatus.

Some improvements have been made in his apparatus by Delplace's patent of 1882 (Ger. P. 23159). He provides a long, flat platinum still with an undulated cover, bearing on the top of the four undulations as many still-heads. From that which is nearest to the acid feed, only water distils off; the others yield water with more and more acid, the fourth rather strong acid. Thus with one pan acid of 98 per cent.  $\text{H}_2\text{SO}_4$  can be obtained. The bottom is best made in a corrugated shape (as in Fig. 401, p. 1131). I am not aware whether this kind of still has been carried out in practice.

The platinum stills built by the Paris firm F. Desmoutis, Lemaire et Cie., as formerly used, before the shallow form had been introduced, are shown in the first edition of this work, Vol. I. pp. 526 and 536. Since 1876 this form has been replaced by

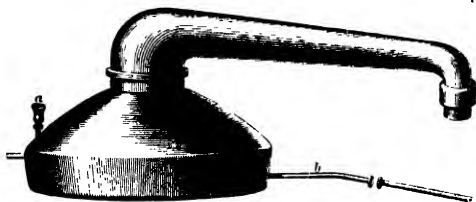


FIG. 407.

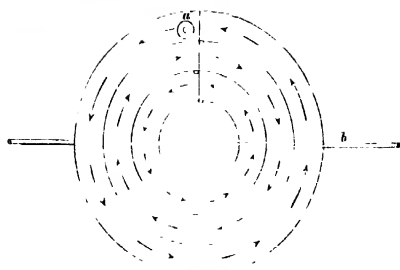


FIG. 408.

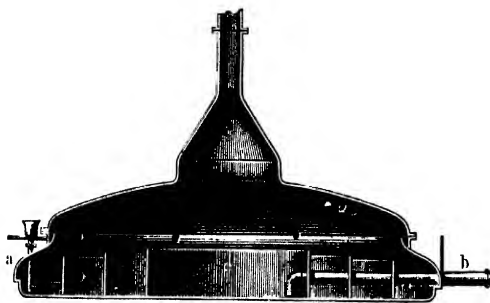


FIG. 409.

a shallow still, as shown in Fig. 407; and this is frequently made with a bottom fitted with concentric partitions, which force the acid to travel through the still in a circuitous way, as indicated by the arrows, and ultimately to flow out through pipe *b*. This is shown in Figs. 408 and 409.

(It must not be overlooked that these partitions are sometimes found to leak, which has caused some manufacturers to abandon this otherwise very rational plan and to return to plain-bottomed stills.)

Figs. 410 and 411 show the setting of these stills, which is extremely simple, the still-bottom resting on a plain cast-iron ring.



FIG. 410.

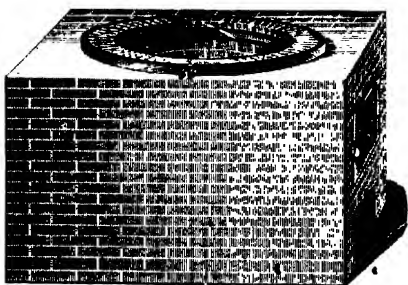


FIG. 411.

Figs. 412 and 413 show a *longitudinal still*, preferred by some French manufacturers, equally provided with partitions. Formerly most buyers preferred the circular shape; now some of them prefer the oblong shape as better utilising the fuel. But common to all are the partitions which cause the acid to flow through the still in a prolonged stream, without any

mixture of the concentrated with the dilute acid. This system has been applied for many years with great success. Where two stills are to be worked in combination a difference must be made between the case where acid of  $65\frac{1}{2}^{\circ}$  B $\acute{e}$ . and that where acid of 97 to 98 per cent. is required. In the former case it is best to place both stills on the same fire. They thus produce

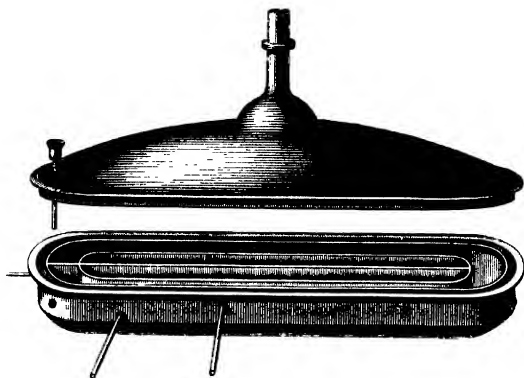


FIG. 412.

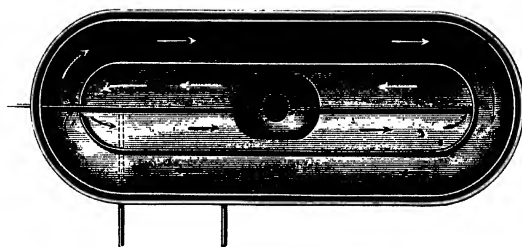


FIG. 413.

slightly less than if fired separately; but this is outweighed by the saving in fuel, labour, and repairs (about 20 per cent. on the fuel and 25 per cent. on labour and repairs). The waste fire-gases cannot concentrate the feeding-acid in the lead pans, which these receive from the chambers (above  $59^{\circ}.5$  B. =  $140^{\circ}$  "w.); but this is an advantage, as the acid gets less charged with lead, and its strength is absolutely regular. The quantity



## 1138 THE CONCENTRATION OF SULPHURIC ACID

of distilling acid is lessened; the finishing-still furnishes a distillate of from  $20^{\circ}$  to  $25^{\circ}$  B $\acute{e}$ . ( $= 32^{\circ}$  to  $42^{\circ}$  Tw.), whilst the distillate from the first still is almost pure water and is thrown away. This combination is shown in Figs. 309 and 310 (p. 709) of our second edition; the two stills, all complete with a Liebig's cooler, weigh 50 or 51 kg. for a production of 10 tons in twenty-four hours.

For concentrating acid up to 97 or 98 per cent.  $\text{H}_2\text{SO}_4$  two stills must be combined, each of them heated by a separate fire.

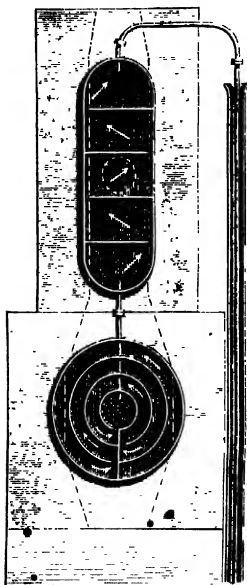


FIG. 414.

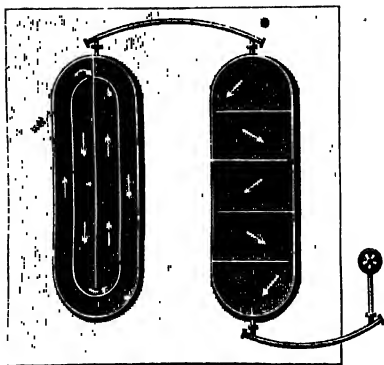


FIG. 415.

(This system, as well as other shapes of these French stills, is illustrated in our second edition.)

Figs. 414 and 415 show the combination of a circular with a longitudinal still, which is said to be especially useful for the production of most highly concentrated acids.

Figs. 416 and 417 (p. 1139) show the combination of two longitudinal stills, one of them (A) with longitudinal partitions and with a recess in the bottom, the other (B) with transverse partitions. C is the platinum cooler.

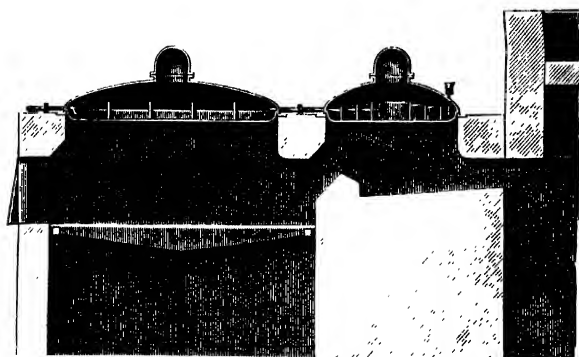


FIG. 416.

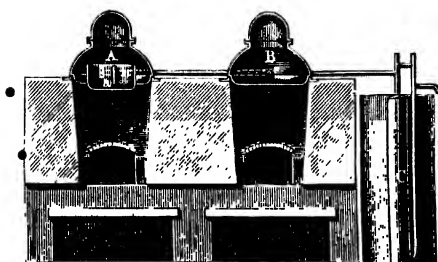


FIG. 417.

Scheurer-Kestner (*Bull. Soc. Ind. Mulhouse*, 1892, p. 321) gives data concerning the difference produced by working with a Desmoutis still, first without and then with concentric partitions, the acid being forced by the latter to remain longer in the stills in the proportion of 48 : 62. The data refer to both styles of work :—

	Without partitions.	With partitions.
Make in 24 hours . . . . .	5136	6632 kil.
Concentration of acid . . . . .	92.5	92.5 per cent.
Average strength of distillate . . . . .	36°	11° Baumé
Weight of ditto . . . . .	2160	2160 kil.
Weight of the corresponding $H_2SO_4$ . . . . .	816	216 „
Percentage of acid distilled . . . . .	15.8	3.2
Weight of coal used . . . . .	1100	1100 kil.
Ditto per cent. concentrated acid . . . . .	21.4	16.5
Water evaporated . . . . .	1344	1944 kil.

These undoubted advantages of the concentric partitions are, however, counterbalanced by a greater loss of platinum and more frequent repairs, so that many manufacturers have abandoned this system after having tried it.

*The way of firing platinum stills* is of the greatest importance, not merely so far as economy of fuel is concerned, but even to a greater extent where it is necessary to manufacture acid of a regular and high degree of concentration. Ordinary hand-fired grates will do quite well where the acid need not exceed 95 per cent.  $\text{H}_2\text{SO}_4$ ; and the waste heat of the flame may be utilised for bringing up the chamber-acid in lead pans to the strength required for feeding the still, say  $140^\circ \text{Tw.}$ , although in most cases this can be equally effected without any cost by the waste heat of the pyrites-burners. But where acid of 96 per cent. is regularly required, it is much better to adopt a plan ensuring perfect regularity of heat; and this becomes indispensable when acid of 97 or 98 per cent. is to be regularly run in a continuous process. This is very easy to understand, for with the very shallow depth of acid now universally employed a slackening of the fire will instantly tell upon the concentration. Supposing the feeding-acid to be of uniform strength (a necessary condition for continuous work), it stands to reason that the strength of the acid run out in a continuous process must vary with the heat employed, and that consequently that heat should also be as uniform as possible. No ordinary fire-grate will fulfil this condition; this may be done by really efficient mechanical stokers; but I am not aware of any case where such have been tried for platinum stills.

Another means for attaining the same end is the employment of good gas-producers, and of these one of the most efficient for the present case seems to be that of G. Liegel, of Stralsund (Prussia). A large number of Liegel producers have been already fitted to platinum stills and have been working for many years past; and I am assured, on most reliable authority, that there is nothing equal to them for obtaining the most highly concentrated acid in a regular way. Figs. 418 to 423 show the Liegel producer as applied to sulphuric-acid stills; but, of course, special modifications must be made in particular cases, as stated by the inventor of the system.

At some factories, where the principal quantity of strong sulphuric acid is made by the contact process (Chap. XI.), platinum stills are employed for producing particularly clear acid, and as cannot be turned out by the contact processes in spite of all precautions.

*Special Methods of Condensation of the Vapours from Concentrating Vessels.*

Dieffenbach (Ger. P. 189863; Fr. P. 371685) separates the vapours formed in the concentration of sulphuric acid by dephlegmation into steam (which escapes) and condensing acid. It is claimed that thus acid of 98 per cent.  $\text{H}_2\text{SO}_4$  can be obtained without any loss of acid in the vapours.

Littmann (Ger. P. 187253) places on the top of the still a condenser, in the shape of a wide-bellied bottle, cooled by water; the top of the vapour-pipe leading into it is closed, and the vapours issue through many holes in the sides, so that they form many jets, striking horizontally against the cooled sides of the condenser. Most of the acid is thus condensed to a liquid which drops back into the pan; the remaining vapours are carried through a pipe placed in the cooling-water. It is claimed that this contrivance does many times the work of horizontal platinum pipes, and that it prevents all trouble by bumping in the course of the distillation.

A. Will (Ger. Patterns No. 416830) has constructed an apparatus for the automatic indication of any acid getting into the cooling-water of acid-condensing apparatus. It consists of two zinc plates, ending above the lid in clamps which, in case of any acid acting on the zinc, gave an alarm in the well-known manner.

*Concentration in Platinum Dishes with Lead Hoods (Faure and Kessler's System).*

The first stills constructed on the principle of combining a platinum bottom-dish, as the only part of the still coming into contact with the hot concentrated acid, with lead covers cooled by water, were used by Messrs Harrison, Blair & Company, of Bolton, and Mr A. Smith, of Dublin, some time before 1860, but were given up again. In 1863 L. Kessler proposed his first still, which was erected at Griesheim (*Dingl. polyt. J.*, vol. clxxvi.

pp. 34 and 164, ccxxi. p. 85). This apparatus was not a success, and was replaced ten years later by the firm of Faure and Kessler, at Clermont-Ferrand, by a new construction which has been gradually changed as more experience was gained. The older forms of the apparatus, which are not used now, are fully described in our first edition pp. 542 to 551, with many illustrations. We shall here only describe the present form of the apparatus, with the aid of detailed drawings to scale, kindly furnished by the proprietors of the patents, Messrs F. Desmoutis, Lemaire et Cie, of Paris, platinum works.

Fig. 424 gives a general sketch of the apparatus on a scale of  $\frac{1}{25}$ . *a* is the platinum basin, with the lead bell *b*, which will be illustrated and described in detail further on. The dilute acid condensing on the sides and top of the bell runs away through pipe *c*. The uncondensed vapours pass away through pipe *d*, which bends downwards and dips into the condenser *e*. The acid formed here, after passing through the hydrometer cylinder *f*, runs away through *g*, together with that from *c*. The cooling-water for the bell enters at *h*, that for the top cover at *i*. The concentrated acid runs away at *k* into the cooler *l*, to be described below, and from this through *m* into carboys, etc.

The fire of the fireplace *n* passes either underneath another or even a third platinum basin, each of them placed so much higher than the preceding that the acid can run from one to another, or else directly under a set of lead evaporating-pans, in which chamber-acid of  $106^{\circ}$  Tw. is brought up to  $142^{\circ}$ , the proper strength for feeding the platinum basins.

Fig. 425 gives details of the condensing-apparatus for the weak acid, which can be understood without further explanation.

Fig. 426 gives a detailed drawing of the dish and bell, on a scale of  $\frac{1}{16}$ . *a* is the platinum basin, the size of which must be proportionate to the production intended. In order to stand the work for a considerable time, it should not be too thin; it is necessary to calculate from 2.9 to 3 kg. of platinum to each ton of 94 per cent. acid made in twenty-four hours. For instance, a basin capable of turning out 5 tons of strong acid per twenty-four hours weighs from 14.5 to 15 kg., and has a diameter of 0.88 m. ( $= 2$  ft.  $10\frac{3}{8}$  in.); for 7 tons of acid it would weigh 20 or 20.5 kg., with a diameter of 1.06 m. ( $= 3$  ft.  $5\frac{3}{8}$  in.); for  $1\frac{1}{2}$  tons of acid 6.5 kg., with a diameter of 0.60 m. ( $= 1$  ft.  $11\frac{3}{8}$  in.).

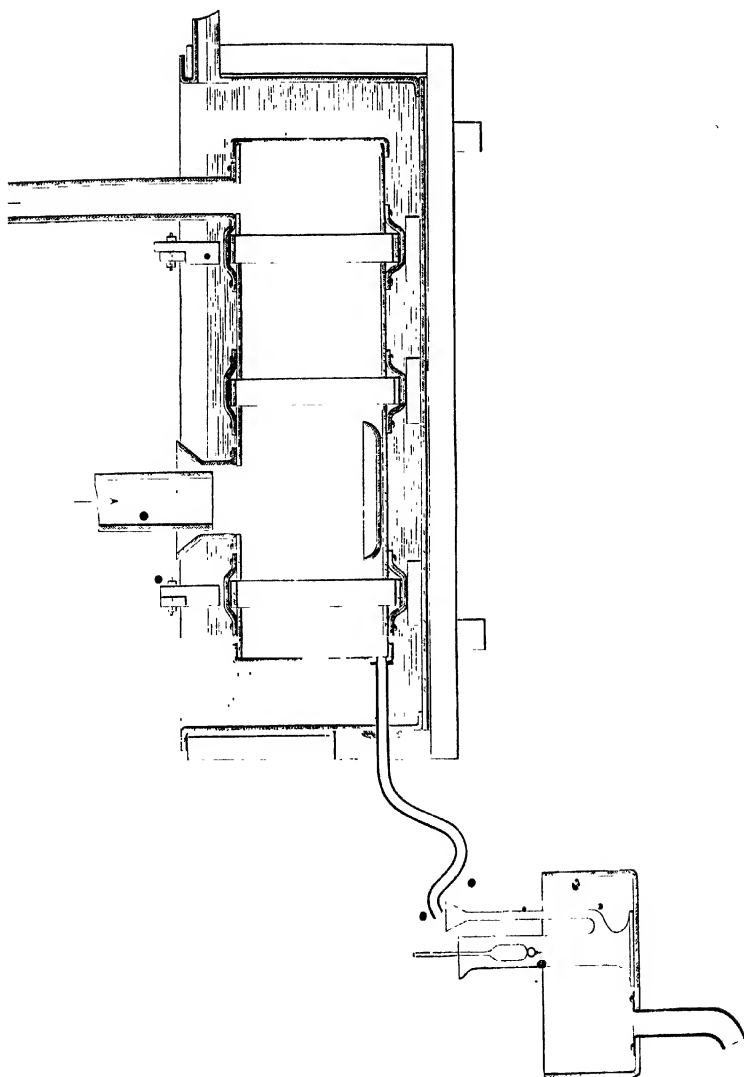


FIG. 425.

The rim of the basin is shaped like a hydraulic lute, *b b*, with the outlet-tube *c* for the dilute acid condensing on the sides of the leaden bell, *g g*; this rim is supported by a cast-iron ring, *f*. Further, there is an outlet-tube, *d*, for the strong acid, and a supporting ring, *e* (of cast-iron), for the lower part of the basin.

The basin is surmounted by a leaden bell, formed of a double-walled cylinder, *g g*, and a double-walled conical hood, *h h*. The cylindrical part is supported on the outside by three iron stanchions, *i i*, and an iron hoop, *k k* (40 × 5 mm.). The

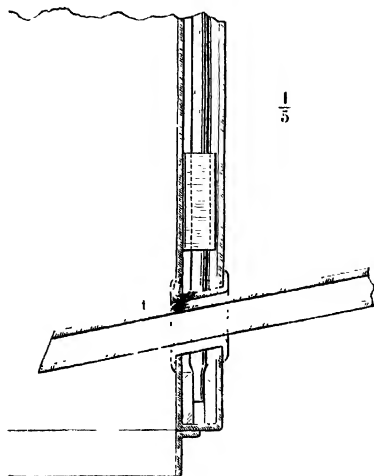


FIG. 427.

pieces *i i* end at the top in hooks, which serve for suspending the bell *g g*, by means of chains.

The diameter of the cylindrical part is 0.870 m. (= 2 ft. 10½ in.) inside and 0.940 (= 3 ft. 1 in.) outside. The inner shell has a thickness of 5 mm. (say 11 lb. per superficial foot), the outer 3 mm. (say 7 lb.). Iron rods, *l l*, ½ an inch thick, held by means of straps, *m m*, form a skeleton frame for stiffening the inner cylinders; they are from 3 to 4 in. apart. The pipe *n* serves for introducing cold water in the bottom of the annular space between the two leaden cylinders; pipe *o* conveys the partially-heated water into the annular space of the conical

hood, *q q*, and *p* is the outlet for the hot water from the latter. Pipe *r* lets off the air escaping from the cooling-water during its passage through *g g*, and pipe *s* serves for the same purpose in the hood *q q*. The arrow *t* shows where the feeding-acid runs in; Fig. 427 gives the detail of this.

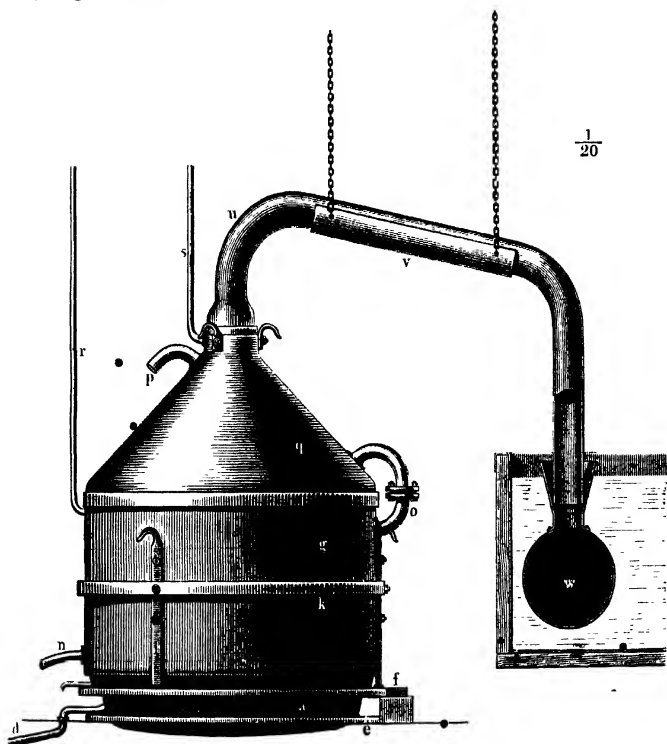


FIG. 428.

The uncondensed vapours are taken away by pipe *u* suspended from the roof by means of the spout *v* (Fig. 428); it dips into the cooler *w*, where the weakest acid is condensed.

Fig. 428 gives a front elevation. The letters all have the same signification as in Fig. 424. (Some other illustrations of this system are given in our second edition.)

The cooler employed by Faure and Kessler for the strong



acid is made of lead, avoiding the use of platinum, and is shown in Fig. 429. A lead vessel, A, stands on an annular lead cylinder, B, whose base *b* is a little widened out for greater stability. In the middle of the height the partition *c* cuts off the top from the bottom cylinder, the hollow space of A still remaining in communication with the annular space of B. All the hollow spaces are filled with acid. On the bottom *c* the

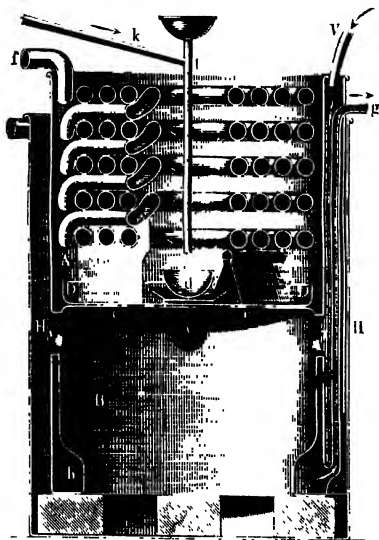


FIG. 429.

shallow lead dish D is placed; and in its centre the porcelain dish *d* receives the almost boiling acid from the platinum tube *k*, so that the hot acid mixes with cooled acid without injuring the lead at the point of contact. In A there are five worms, *s s*, connected with each other and constantly fed with cold water, which runs off heated at *f*. The whole cooler stands in a cylindrical vessel, H, also constantly supplied with cold water through V; the latter, therefore, always fills the inner space *b* of the annular vessel B, circulating through the openings

11. Since the acid entering through the tube *t* is much hotter than that into which it flows, it rises to the top, comes into contact with the worms *s s*, and is partly cooled; it then flows downwards along the sides, and passes into the annular space *b*, where it only forms a thin layer and is further cooled. At last it rises up in the pipe *g*, and from this runs into the carboys. As the diameter of the vessel is about 3 ft. 3 in., the stream of acid moves very slowly in it, and there is time for cooling. A cooler of the above diameter and equal height suffices for 100

carboys of acid per diem. This apparatus is very ingeniously constructed, but rather complicated. It requires an excellent plumber and incessant cooling with cold water; otherwise it would be very soon destroyed.

For cooling the hot acid the quartz-glass apparatus ("vitrosil") of the Deutsche Ton- u. Steingewerke in Charlottenburg has been very advantageously employed, both in the shape of pots and of coils (Pohl, *Z. angew. Chem.*, 1912, p. 1852).

A weak part of the apparatus consists of the lead hoods. The Chemische Fabrik Rhenania (Ger. P. 64572) makes these hoods of a long coil of lead tubing, burning the walls together so as to form a tight bell, within the walls of which the cooling-water circulates. This system answers very well, and has been introduced at a number of factories. It is probably the best now in existence for this special purpose.

The principal feature of the work with the Faure and Kessler stills is this—that the acid, coming hot from the leaden evaporating-pans, is continuously run into the platinum basin, or the first of a set of two or three such basins, where it stands in a very shallow layer (2 or 3 in. deep), and is exposed to the direct action of the fire playing upon the whole of the bottom of the dish. This causes such rapid evaporation that the acid, issuing at the side opposite to that from which it had entered, and from the bottom of the still, flows out in a sufficiently concentrated state. The amount of work done is proportionate to the size and number of the platinum basins. The mixed vapour of acid and water formed in the basins, as it rises up, strikes against the water-cooled sides and top of the leaden hood, and is there condensed to dilute acid, running down the sides and forming a hydraulic lock between them and the platinum dish; an overflow (at *c*) carries it outside, and prevents it from getting back into the platinum basin. The water cooling at the same time prevents the leaden hood from being damaged by the joint action of heat and acid vapours.

The cost of fuel is not perceptibly different with Faure and Kessler stills from that of ordinary platinum stills; and the large quantity of water required for cooling-purposes in the former system is an item of cost to be put against the saving

which attends the cost of plant. It was urged by the inventors as a great advantage of their plan that the loss of platinum is much less than with stills made entirely of platinum; but this is very doubtful, as the wear and tear of the platinum occurs almost entirely in the places which are in contact with the fire-gases, and which are equally large in both systems; and any slight loss of platinum in the other parts of ordinary platinum stills will cost hardly less than the repairs of the very complicated leaden hood and connections of the Faure and Kessler system. According to information from Messrs Desmoutis, Lemaire et Cie, the bell and hood last about two years, and must then be replaced.

I have also obtained the following data from the same firm. The plumbing work for a F. and K. apparatus turning out 5 tons of acid of 168° Tw. per diem amounts to about 1200 francs, viz. :

	francs.
For the bell itself . . . .	450
For the acid-cooler . . . .	350
For the vapour-condenser . . . .	250
For sundries . . . .	150
	<hr/> 1200

or about 1 franc per kg. of the lead employed.

The consumption of cooling-water averages 3 tons per hour, or 75 tons per day.

The consumption of fuel is from 18 to 20 per cent. of the acid manufactured.

The great saving in prime cost caused a rapid spreading of the Faure and Kessler system, especially in Germany, Austria, and America, much less in France and England. But since the ordinary platinum stills (owing, no doubt, to the stimulus given to the makers by the new system) were considerably improved, and were constructed of much lighter weight and cost for the same output than formerly, and since the drawbacks of constant repairs, of the great amount of water required, and the frequently minor strength of the acid produced in the Faure and Kessler stills became more perceptible, the latter system has again receded into the background, although, of course, the apparatus once erected are still kept at work. There are probably few new stills constructed according to this system, and several manufacturers who had put up this apparatus have replaced it by ordinary

stills.<sup>1</sup> The enormously increased price of platinum might give a new impetus to the Faure and Kessler system, if L. Kessler's own new hot-air apparatus did not seriously compete with his former invention (*cf.* p. 1191). It must not be overlooked that the strength really attained by it rarely exceeds 93 per cent.  $\text{H}_2\text{SO}_4$ , or at the very most 96 per cent.; with higher strengths the lead hood is acted upon to a perceptible extent.

*Other forms of Platinum Stills.*

We here briefly quote a number of patent constructions none of which have found any, or only very little, application beyond the places where they originated.

A still constructed by F. W. Kalbfleisch is figured and described in our second edition, pp. 722 to 724. It was patented in Germany in 1877 (No. 1005), and improved as described in Amer. P. 267221 (*J. Soc. Chem. Ind.*, 1883, p. 42). Other American stills are those of M. Willett (B. P. 9362 of 1884); C. Bartsch (B. P. 6127 of 1885). We mention also H. Glover's platinum dish, placed within the gases of a brimstone-burner as shown, p. 404.

Siebert (B. P. 9514 of 1893) built platinum retorts with stepped bottoms, on which the acid runs down in cascades. [The rate of concentration and the consumption of coal are very favourable in this apparatus; but it has been abandoned, as the bottom could not be prevented from running dry, and thus the wear and tear became too great.]

Hannetelle (B. P. 22704 of 1891) describes four cylinders mounted stepwise, inclined alternatively to opposite sides, the acid running downwards through all of them. The "Chapuis still" is constructed on the same principle.

Lasne uses a flat, oblong still, 6 ft. 6 in. long, in which the acid runs from one end to the other in a layer of about 2 in.

Howard (B. P. 1762 of 1897) describes an automatic apparatus for regulating the strength of the acid flowing out of the platinum stills.

England (B. P. 22715 of 1895) employs the heat of the out-flowing acid usefully, by cooling it with the fresh acid to be concentrated.

<sup>1</sup> This is confirmed by information received from platinum-smelters in 1902.

*Loss of Platinum in the Concentration of Sulphuric Acid.*

This is a very important matter, on which the first accurate observations were made by Scheurer-Kestner in 1862 and continued for many years. Detailed statements regarding this subject are given in our second edition, pp. 725 to 727. Here we give only a brief abstract.

In the presence of small quantities of nitrogen acids, the loss is from 2 to 3 g. platinum per ton acid of 93 to 94 per cent.  $\text{H}_2\text{SO}_4$ , in the absence of these (removed by ammonium sulphate) only a little over or under 1 g. "Extra-concentrated acid" (97 to 98 per cent.  $\text{H}_2\text{SO}_4$ ) entails a loss of 6 to 8 g. platinum per ton. The head, siphon, etc., also suffer a loss of weight.

Hasenclever states the loss of platinum when using acid free from nitrogen compounds = 0.25 to 0.97 g. per ton of acid. At Uetikon a Faure and Kessler apparatus lost 0.75 g. per ton of ordinary acid; when making the strongest acid the loss amounted to 10 g. per ton of acid.

Davis (*J. Soc. Chem. Ind.*, 1894, p. 210) states that the loss of platinum sometimes goes down to 0.34 g. per ton. Formerly it was less than it is now [?]. When making 97 per cent. acid the loss occasionally rises to 20 g. platinum per ton (*vide infra*).

The following information was obtained in 1902. A collection of statements emanating from a number of firms, made by W. C. Heraeus, shows the loss of platinum per ton of strong acid manufactured as follows:—

- (1) Concentration to 92 per cent.  $\text{H}_2\text{SO}_4$ , from 0.18 to 0.78 g.
- (2) Concentration to 93 to 96 per cent.  $\text{H}_2\text{SO}_4$ , from 0.30 to 1.3 g.
- (3) Concentration to 97 to 98 per cent., 1.9 to 3.0 g.

Contrary to the ordinary statement in chemical text-books, Conroy (*J. Soc. Chem. Ind.*, 1903, p. 455) has found that sulphuric acid, even when pure, exerts a marked solvent action upon platinum. In fact the quantity taken up by acid of 95 per cent.  $\text{H}_2\text{SO}_4$  at 250° C. far exceeds that observed in practice. This is explained by the fact that reducing substances, like  $\text{As}_2\text{O}_3$ , S,  $\text{SO}_2$ , and even  $\text{N}_2\text{O}_3$ , retard the solvent action. Nitric acid does not promote it directly, but in practice it is injurious because it oxidises the reducing-substances present. Ammonium,

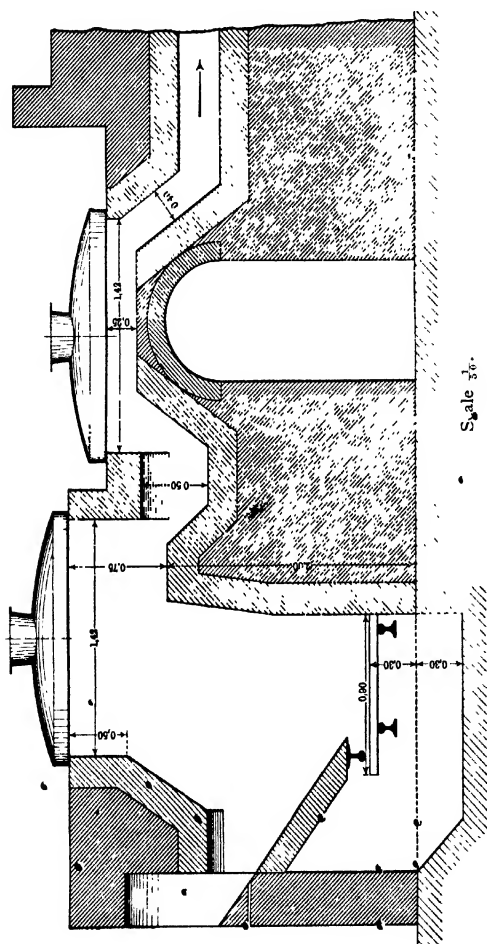
ferrous and ferric sulphate, sodium chloride and nitrate, have no action. The greater destruction observed when bringing the acid to higher concentration is not due to that concentration itself, but to the higher temperature necessary for it. Délépine (*Comptes rend.*, 1905, cxli. pp. 886 and 1013) also found a very slight action of pure concentrated sulphuric acid on pure platinum foil at temperatures of, say,  $250^{\circ}$  to  $270^{\circ}$ , but decidedly more at the boiling point ( $338^{\circ}$ ). If the boiling temperature is raised by adding potassium sulphate, say to  $350^{\circ}$  to  $355^{\circ}$ , the loss of platinum amounts to 0.04 to 0.05, at  $365^{\circ}$  to  $370^{\circ}$ , 0.12 to 0.13 per superficial decimetre per hour. Absolutely pure acid acts quite as much as such containing 0.1 per cent.  $\text{HNO}_3$  and upwards. The presence of  $\text{NH}_4\text{Cl}$  sensibly lessens the attack. Quennessen (*ibid.*, cxlii. p. 1341) examined the behaviour of platinum (pure and technical) against sulphuric acid at  $400^{\circ}$ . He concludes from his results that in the case of concentrated commercial acid the atmospheric oxygen acts as an oxidiser, but in that of acid containing  $\text{SO}_3$ , this furnishes the oxygen. Le Roy M'Cay (*Chem. Zeit.*, 1912, p. 1072), on the contrary, found that platinum is acted upon by boiling sulphuric acid even in the absence of oxygen, e.g., in a current of carbon dioxide. This action is prevented by  $\text{SO}_2$ ,  $\text{As}_2\text{O}_3$ , or  $\text{Sb}_2\text{O}_3$ .

In Knocke's description of the Oker works (*Dingl. polyt. J.*, cliv. p. 181) it is mentioned that formerly the platinum stills used to be fired with coals, but that wood had been introduced instead, because the still was found damaged in consequence of the sulphur contained in the coals. Even by the formation of carbon-platinum the platinum may become brittle; the fuel, therefore, ought never to come into immediate contact with it.

Undoubtedly the durability of platinum stills is greatly influenced by the way they are set and worked. If the stills are placed too near the fire-grate, or if the flame is sooty, compounds of platinum with carbon, silicon, and hydrogen are formed, which make it crystalline and brittle and impart a rough surface to it. In this respect gaseous fuel is superior to every other kind of firing (*cf.* p. 1140).

Fig. 430 gives an idea of the way in which platinum stills can be set so as to avoid all risk of damage by silicates from the coal-ashes being projected against the pan-bottom, or other damage by the fire (received from Mr W. C. Heraeus, Hanau).

*Mercury* is sometimes contained in blende, etc., and gets into sulphuric acid (p. 1040). If it reaches the platinum stills



it may do great harm, as it may there be reduced to the metallic state.

*Prices of Platinum Stills.*—Hasenclever (*Chem. Ind.*, 1892

p. 30) gives the following table of prices (in marks) of platinum stills per kilogram (the mark = nearly 1s.) :—

Year.	Marks.	Year.	Marks.	Year.	Marks.
1869	600	1877	798	1885	1040
1870	600	1878	825	1886	1040
1871	600	1879	900	1887	1040
1872	600	1880	880	1888	1080
1873	837	1881	880	1889	1107
1874	837	1882	890	1890	1970
1875	800	1883	947	1891	1650
1876	800	1884	1013	1892	1250

Since then the prices of platinum (to which about 25 marks per kilogram must be added for workmanship in the case of platinum stills) have been :—

Year.	Marks.	Year.	Marks.	Year.	Marks.
1893	1300	1900	2450	1907	3650
1894	1300	1901	2600	1908	2400
1895	1500	1902	2600	1909	3700
1896	1600	1903	2500	1910	6000
1897	1650	1904	2650	1911	6100
1898	1800	1905	2800	1912	6667
1899	2200	1906	5000		

The greatest production of platinum in the Ural district occurred in 1901, and amounted to 203,000 oz. It declined to 56,000 in 1908, and in 1910 rose again to 175,000 oz. The enormous rise of prices is mostly explained by the continuously deteriorating quality of the ores. The principal beds are now exhausted.

#### *Gold-lined Platinum Stills.*

W. C. Heraeus, of Hanau, found that *gold* resists boiling sulphuric acid much better than platinum. He quotes the following figures, putting the loss of weight of chemically pure platinum = 100 :—

Technically "pure" platinum	90
Alloy of 90 platinum + 10 iridium	58
Pure gold	13

Which means that pure gold suffers only one-seventh as much as technically pure platinum.



Since pure gold was formerly too dear for manufacturing stills (nowadays it is worth only half as much as platinum for the same weight!), Heraeus prepares platinum coated with a firmly adhering layer of gold in the following manner (invented by his chemist, Dr Kuech):—An ingot of platinum is brought to a white heat exceeding the melting-point of gold, then a quantity of melted pure gold corresponding to the desired thickness of the coat is poured over it, and the double ingot thus formed is rolled into a sheet. Such sheets are made of the following thicknesses:—

0.4 millim. platinum	0.05 millim. gold.
0.4           "           "	0.1           "
0.3           "           "	0.2           "

Both under the hammer and in the fire these double sheets behave exactly like one metal; they are easily soldered with sheet platinum by means of gold, the operation being conducted in such a manner that the layer of gold is melted only at the soldering joint. It is not possible to substitute a cheaper metal for platinum (as, for instance, proposed by Neuerburg, Ger. P. 58511), since in this case the slightest injury to the layer of gold would make the apparatus entirely useless, repairs being out of the question. These gold-plated platinum bottoms are especially useful in the manufacture of the strongest (97 to 98 per cent.) oil of vitriol, in which the platinum is energetically acted upon.

According to statements collected by Mr Heraeus from various firms, the loss of weight in his platinum-gold stills per ton of strong acid made (*cf.* similar statements concerning ordinary platinum stills, p. 1150) has been: (*a*) in the manufacture of 92 per cent. acid, from 0.011 to 0.072 g.; (*b*) in the manufacture of acid of 93 to 96 per cent., from 0.03 to 0.138 g.; (*c*) in the manufacture of acid of 96 to 97 per cent., from 0.17 to 0.205 g.; (*d*) in the manufacture of acid of 97 to 98 per cent., from 0.040 to 0.26 g.

Since 1891, when these apparatus were first brought out (Ger. P. 63591), up to the beginning of 1902, 73 platinum-gold stills have been sold to 16 works in Germany, 18 to 7 works in Austria, 21 to 8 works in America, 7 in Russia, 3 in Switzerland, 2 in Belgium, 2 in Sweden, 1 in Italy, 9 in South Africa.

At one of the German factories the first of these stills was put up in January 1891, and is in use now; a large number of stills of the same kind has since been added.

Heraeus (in *Z. angew. Chem.*, 1903, p. 1201) defends his system against some observations made upon it by Hartmann and Benker (*ibid.*, p. 1154).

The Heraeus platinum-gold combination may be regarded as the best kind for apparatus where *strong* and *pure* acid is concerned, both for entire stills and for pans covered with leaden hoods. The gold coating in the former case must be extended to the whole interior of the boiler, not merely to the bottom, as otherwise galvanic action sets in at the place where the acid touches both platinum and gold. The Heraeus composition is not adapted for impure acid, which forms crusts, as these necessarily cause damage to the gold, and as soon as any platinum is exposed the galvanic action sets in. Otherwise it is excellent.

It should be noticed that ordinary goldplating, whether by electroplating or by the igneous method, does not fulfil the object of protecting the platinum, as practical tests have repeatedly proved. No doubt such gilding is always more or less porous, so that galvanic action with the sulphuric acid sooner or later sets in and injures the metal. This is not the case with the compact sheet of gold, rendered completely dense by rolling the Heraeus bars to the required thinness.

In August 1911 I received the following information on that subject from the W. C. Heraeus Co. The platinum-gold apparatus have been introduced for the manufacture of high-grade acid almost everywhere in Germany, and to a considerable extent in North America. They have answered in every respect. About five years ago, when the price of platinum had approached £250 per kilogram, several factories sold their platinum apparatus and replaced the upper part by an alloy of 90 gold + 10 platinum; the lower part, which is surrounded by the fire-gases, being made as before of a composition of equal parts of platinum and gold, soldered together by the patented Heraeus process. Formerly the upper part had been made of a composition of about 4 platinum + 1 gold, but it is now preferred making it of gold, alloyed with 10 per cent. platinum, in order to make it harder and to permit soldering it with

pure gold. This kind of apparatus has also answered perfectly, and is still at work at Griesheim and at Aussig. To be sure, the number of acid-concentrating apparatus made of platinum or gold diminishes from year to year, and in a few years such apparatus will be found at work only in such cases where exceptionally pure and clear acid is called for.

The price of gold may be assumed to be always the same, viz., 3000 marks per kilogram; therefore until the year 1905 it was dearer than platinum for the same weight, but since 1906 the state of matters in that respect is quite different, as appears from the table of prices given on p. 1153.

#### *Crusts forming in Platinum Stills.*

The iron salts contained in the chamber-acid in concentrating are precipitated as anhydrous *ferric sulphate*, which, being insoluble in strong sulphuric acid, partly attaches itself in white crusts to the vessel, partly remains suspended in the acid in shining flakes: the precipitate also contains a little lead. When it occurs in large quantities it may occasion stoppages of work and also make the acid more or less unsaleable. This especially happens when Glover-tower acid is employed for concentration. In order to remedy this, Gerstenhöfer suspended a large porcelain dish in the still by means of platinum wires, completely immersed in the acid, in which, owing to the boiling movement, all crusts, etc., collect. The dish is taken out from time to time, which can be done very quickly (Bode, *Beitrag*, 1872, pp. 50, 51). This arrangement seems to have been introduced in very few places, if at all. So much is certain, that hardly anywhere can Glover-tower acid be used for manufacturing "rectified oil of vitriol," and that the acid for this purpose is always obtained by a preliminary concentration of chamber-acid, which has not passed through the tower, in leaden pans, either by special fires or by steam-coils, or, more often and rationally, by the waste heat of the burner-gas, or by that of the stills themselves, as already frequently mentioned. In any one of these ways the acid is brought up to about 140° Tw. without having been in contact with the flue-dust from the pyrites-burners, which contaminates it with a comparatively large quantity of iron.

Even at factories where brimstone is burned the Glover-

tower acid has not been found suitable for platinum stills, because it evidently dissolves too much iron (and alumina) from the "packing" of the tower.

But even with feeding-acid concentrated by bottom-heat only, the precipitation of salts in the platinum stills can be very rarely avoided, if the concentration proceeds beyond, say, 92 per cent.  $\text{H}_2\text{SO}_4$ . Wherever stronger acid is made, it becomes necessary to clean out the platinum stills from time to time, in order to avoid the formation of hard crusts, which would speedily ruin the still. This cleaning is effected by running the still as nearly dry as its form permits, and dissolving the salts by means of hot water or hot weak acid.

This operation has to be performed at various intervals, according to the circumstances of the case. Whilst at some works it has to be done every few days, the stills may elsewhere run on for several weeks or even months.

The following is the composition of crusts formed in platinum stills, as observed at a French works, according to private information:—

	Hard, stony crust.	Softer crust, impregnated with acid.
$\text{Fe}_2\text{O}_3$ . . . . .	33.60	23.00
$\text{SO}_3$ . . . . .	63.20	63.60
$\text{SiO}_2$ . . . . .	...	0.20
$\text{CaO}$ . . . . .	trace	1.10
$\text{MgO} + \text{Na}_2\text{O}$ . . . . .	"	0.85
$\text{As}_2\text{O}_5$ . . . . .	"	trace
$\text{PbSO}_4$ . . . . .	"	"
$\text{Se}$ . . . . .	"	"
$\text{Al}_2\text{O}_3$ . . . . .	"	...

At Stolberg alumina is always found, sometimes exceeding the proportion of iron (1902).

An explosion on cleaning out a platinum still has been reported by Kuhlmann, jun. It occurred by running water upon some acid left in the still (the two strata evidently remaining separate) and starting the fire. At a certain point the two strata must have become suddenly mixed; and the explosion occurred through a violent evolution of vapour (*Bull. Soc. Chem.*, vol. xxxiii. p. 50).

*Concentration in Iron Vessels.*

The great cost of platinum, and the liability of glass to breakage, together with the usually great expense for fuel in the latter case, have led to employing iron vessels for the concentration of sulphuric acid, as it is well known that iron resists strong acid, although it is so very rapidly dissolved by weaker acid. The behaviour of cast (and wrought) iron against sulphuric acid has been described *supra*, pp. 320 *et seq.*

For some time past *cast-iron vessels* have been in constant use for concentrating sulphur acid up to the high strength required, especially for the manufacture of nitroglycerine and pyroxyline, say 98 per cent.  $\text{H}_2\text{SO}_4$ . This strength cannot be attained at all on a manufacturing scale in glass retorts, and in platinum vessels it causes an excessive wear and tear. Moreover the deposits formed in the latter, especially when re-working the spent acid of previous operations, are almost unbearable. There is, therefore, a special inducement for employing cast-iron vessels for this purpose, and this is frequently done. The principal condition is this, that cast-iron is not employed *below a certain strength of acid*. It would appear that this strength is best 93 or 94 per cent.  $\text{H}_2\text{SO}_4$ . Up to this point, then, the acid is brought in glass or in platinum; but beyond this cast-iron vessels may be employed, if certain precautions are observed. In some places they put in a little sulphate of soda which is believed to preserve the iron. In other places they employ long pans (about 10 ft. and 2 ft. deep), covered with a leaden dome, in which the acid (not below 96 per cent.) is heated to  $240^\circ$ . At one end a stream of (heated?) air is blown in; at the other end the acid vapours escape by a lead tube into a lead condenser. The constant change of air allows of bringing the strength up to 98.5 per cent. At the end of the operation, when drawing off the concentrated acid, enough is left in to yield acid of not less than 96 per cent. when feeding with ordinary acid of 93 or 94 per cent. The iron is certainly acted upon, and deposits of anhydrous ferric sulphate are formed; there are also black particles (probably graphite) floating in the liquid. These particles, however, are removed without any special effort by the lead sulphate forming on the leaden cover and falling into the acid, as the sulphate carries

down the black particles. (Cf. p. 1180 on the sketch of such a pan as used for the recovery of acid from "acid-tar.")

In other places they employ pans with rounded corners, of 6 ft. 6 in. by 3 ft. 3 in. by 1 ft. depth, with a rebate round the top, into which fits a shallow inverted pan provided with three necks (one for feeding, two for the acid vapours). The joints are made good with a mixture of asbestos and silicate-of-soda

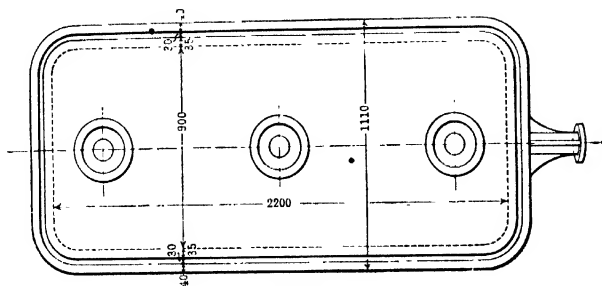


FIG. 431.

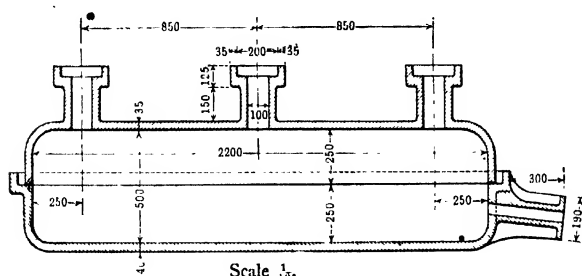


FIG. 432.

solution. Near the bottom there is an outlet-pipe for the acid. The pans are surrounded all over by fire-flues, which keep even the covers hot. Two such pans, placed terrace-wise, and weighing about 7 tons, inclusive of connections, are said to produce (from acid of 142° Tw.) 4 tons of 98 per cent. acid per day, with an expenditure of 25 or 27 per cent. of coals.

Figs. 431 and 432 show the cast-iron retorts usually employed in Germany. Each retort weighs about 2600 kil.; they last about four months. Francke (*Fischer's Jahreshes.*, 1898, p. 329)

states that they concentrate up to 140 tons (?) acid from 93 to 97 or 98 per cent.  $\text{H}_2\text{SO}_4$ , each ton dissolving about 100 g. iron, with a consumption of 28 or 30 per cent. fuel.

Tate mentions pots, 9 ft. wide and 6 ft. deep, 2 in. thick, with cast-iron lids, weighing 11 or 12 tons, in which acid of sp. gr. 1.74 is concentrated within twenty-eight or thirty hours to 96 per cent.; one such pot produces 12 tons of acid. It is allowed to settle and cool for twelve hours, so that one of these pots can be finished every two days. Coal used, 2 cwt. per ton; wages, 1s. per ton; wear and tear, 3s. or 4s. per ton, of finished acid. From time to time the mud consisting of iron salts must be cleaned out, and this represents 4 or 5 per cent. of acid lost. Such a pot costs £60, the lid (which lasts for 3 or 4 pots) £10, the setting £30. Every pot produces from 500 to 600 tons of acid, and is then worth £10 or £15 as old metal. The plant requires very little space and no expensive building. The dirtiest acid can be worked up which can hardly be worked by any other system, and the highest strength can be attained [but the acid will be very impure].

In my report on a visit to America (*Z. anorg. Chem.*, 1894, p. 135) I have described the following plants:—In one place they concentrate the acid to  $66^\circ \text{Bé.} = 93.5$  per cent. in platinum, above that, up to 98 per cent., in round cast-iron pans, 3 ft. wide and 2 in. thick, with double flange for a hydraulic joint, in which a water-cooled leaden hood dips. The hydraulic flanges are lined inside with lead, as they are filled with weak acid. Such a pan lasts two months.

At another place they employ a set of three pans: one is made of cast-iron, 4 ft.  $\times$  3 ft. area, and two of platinum, all three with lead hoods on the Faure-Kessler principle (*cf.* pp. 1142 *et seq.*). In the platinum pan the acid rises to  $65\frac{1}{2}^\circ \text{Bé.}$ , in the iron pan to  $66^\circ \text{Bé.}$  This acid is only used for purifying petroleum. All three pans are heated by heavy petroleum (sp. gr. 0.833, the residue from the manufacture of paraffin), injected by a steam-jet. The regularity and facility of this kind of heating compensate the excess of cost of coal. The flame, after heating the three pans, passes above the weaker acid contained in two lead pans, each 30 ft. long and provided with an inner dry wall and a water-jacket as protection against being burnt through. The first lead pan receives chamber-acid of  $53^\circ \text{Bé.}$ ; the second

lead pan brings it up to 61° Bé., the second platinum pan to 65°·5, the iron pan to 66° Bé. Every set furnishes daily 500 carboys, or about 20 tons, with a consumption of 900 American gallons, or a little over 3 tons, of heavy petroleum, costing 2 cents per gallon, or 7·5 tons per 100 tons acid. The iron pans last three months.

At another place they have two platinum pans with lead hoods, the upper (weak) pan receiving the direct fire, combined with two specially fired iron retorts, constructed as described, p. 1159, viz., a bottom part, 8 ft. × 2 ft. section and 8 in. deep, connected by a flange and rust-joint with a similar shaped, but only 4 in. deep lid. The fire plays all round, first underneath the pan and then above it, in a 12 in. wide flue. The 6-in. vapour-pipe passes through this. The acid attains to 98 per cent., and is drawn off by means of an iron tap.

In a fourth factory, at Pinole, Cal., there is the following apparatus, for the drawings and description of which I am indebted to the superintendent, Mr W. R. Quinan (later on at the De Beers Explosive Works, Cape Town). Fig. 433 (p. 1162) shows the iron pan without cover, seen from above; Fig. 434 is a sectional plan through A B, showing the steam-pipe and the outlet-pipe with mud-box; Fig. 435 part of the longitudinal section through C D, showing the acid-inlet and the thickened bottom below it; Fig. 436 a cross-section at right angles through the inlet. The pan is divided into three compartments by longitudinal partitions, which leave openings at alternate ends of the pan, and thus compel the acid to travel in a zigzag manner. Corresponding to these channels, the pan-bottom is bulged outwards, in order to enlarge the heating-surface. The flat cover rests on a rebate formed on the upper edge of the pan, and is luted in this with a mixture of barytes and silicate of soda; it is held in its place by six castings, *a a*, wedged against corresponding lugs, *b b*, on the pan; these lugs also serve as bearers for the pan. The cast-iron vapour-pipe *c*, 2½-in. bore, is connected by flanges and screw-clamps with a neck formed in the cover; the joint is made by an asbestos washer and the silicate-of-soda mixture. During work the pan-lid is tightly covered with asbestos waste, to protect it against cooling and the consequent action of the acid. The acid-inlet is not arranged in the cover, but in a cup, *e*, cast on



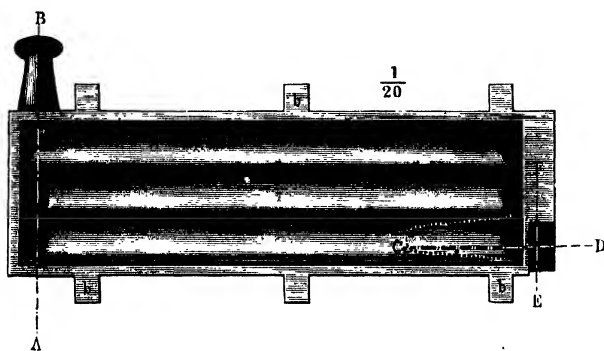


FIG. 433.

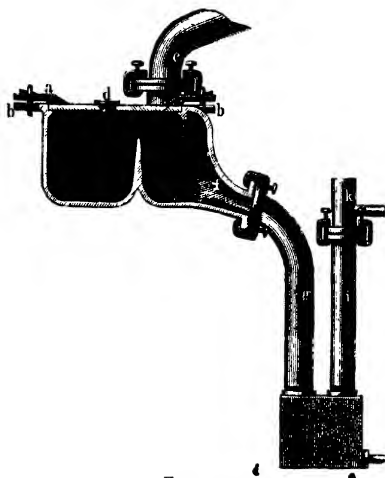


FIG. 434.



FIG. 435.



FIG. 436.

to the pan; below this the pan-bottom is thickened, as this part is always strongly acted upon. The pans are 5 ft. 6 in. long, 1 ft. 6 in. broad, and 10 in. deep; the channels are 5 in. wide each, thickness of metal  $\frac{5}{8}$  in.

The acid-outlet is at the cast-iron neck, *f*, opposite which is a cleaning-hole in the pan-lid, with the cover, *d*, luted by silicate-of-soda cement. Neck *f* is joined to the cast-iron pipe *g*, leading to the mud-box, *h*; from this a cast-iron pipe, *i*, again rises upwards, and is connected by a side-branch with the short platinum tube *k*, which conveys the acid into a Johnson and Matthey's platinum cooler. By this arrangement the acid is obtained perfectly clear and free from mud.

This iron pan is connected with two Delplace platinum stills, 18 in. wide and 5 ft. long. The acid enters 62° B $\acute{e}$ . strong from the lead pans into the first platinum still. The fire, on leaving the platinum stills, travels underneath seven lead pans; there are also lead pans on the eight sulphur-burners. This set of one cast-iron pan and two platinum stills, together with an auxiliary iron pan and platinum stills, supplies a set of chambers of 200,000 cub. ft.

The firing of both iron and platinum stills is performed by crude petroleum, sprayed by superheated steam. The introduction of this system, in lieu of a coal-fire, has not merely saved labour, but also increased the turn-out from 9 tons to 13½ tons of 96 per cent.

The duration of an iron pan is from four to eight months. They are rarely used up, but they crack in the places where thick crusts are formed, sometimes without apparent cause, probably in consequence of faults in casting. [Recently chilled cast-iron seems to have given great satisfaction.] Small holes sometimes forming at the inlet can be stopp'd up by silicate-of-soda cement. The vapour-pipe, *c*, leads to a condenser constructed of platinum and lead. Formerly it had to be protected against cooling and quick corrosion by a thick asbestos coating; but later on a cast-iron mixture was invented which lasts almost indefinitely even without such protection [probably chilled cast-iron].

During the work a *deposit* is formed at the bottom, principally consisting of ferric sulphate, which is removed once a fortnight. The pan is emptied, the cover removed

the outlet *f* is closed, the pan is filled with water and heated to boiling. The crusts, which are sometimes  $\frac{1}{2}$  in. thick, are then chiselled off. Such crusts of course greatly diminish the heating efficiency. In the first channel, where the fresh acid enters, there is not much deposit—on the contrary, the iron is slightly acted upon; and the ferrous sulphate, together with that issuing from the chambers in large quantities (*cf.* below), is deposited in the second and third channels. A little mud is always carried along by the acid, but is deposited in box *h*.

The acid made by this apparatus, remarkable to say, contains less iron than that formerly concentrated to 96 per cent. in platinum stills at the same works. No doubt this is caused by the fact that they now bring up the acid to 97 or 98 per cent., which causes the ferric sulphate to crystallise out. But it is possible to turn out 95 per cent. or even 94 per cent. acid in this apparatus.

As to the consumption of fuel, more is used with iron pans than with platinum stills. Formerly the consumption of coal for making 96 per cent. acid in platinum stills, inclusive of chamber-steam, was 22 per cent. of the acid; now, for making 97 per cent. acid in iron pans it is the equivalent of 28 to 30 per cent. of coal (used in the shape of petroleum).

At the same works they treat a large quantity of *waste acid from the manufacture of nitro-glycerine*. This after denitration yields acid of 53° Bé., which was formerly concentrated in special top-fired lead pans, and subsequently in the above-described combined iron and platinum stills. But as the mixed acids are sent backwards and forwards in sheet-iron glycerine drums and take up much iron from these, the denitrated acid is now run into the chambers, where much of the mud is deposited, and the chamber-acid is then treated as above. Such acid could not possibly be concentrated in platinum stills alone, on account of the crusts.

Scheurer-Kestner (*Bull. Soc. Ind. Mulhouse*, 1892, p. 348) employs the following connection between the iron pan and a platinum lute for receiving a Faure\* and Kessler hood (Fig. 437). *F* is the cast-iron pan, resting on the brickwork by means of the flange *L*. *a, b, c, d*, is the platinum rim, to which is soldered a flange, *g*; *h*, held between the flange *K*, cast on the pan *F*, and a loose iron flange, *i, i*, the joint being

made with asbestos or gypsum pipeclay and secured by screw-bolts. The apron *g, a*, forming part of the platinum rim, protects the cast-iron from the drops of weak acid falling from the top. A cast-iron pan supplying 5 tons of acid in twenty-four hours weighs 5 cwt.: it yields on the average

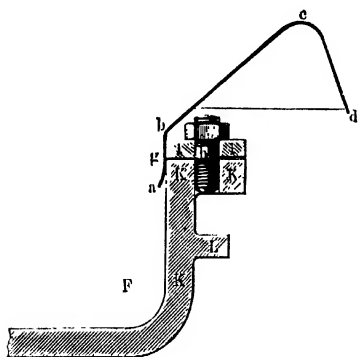


FIG. 437.

12.7 g. iron to 100 kg. acid concentrated from 92.5 to 96 per cent. The platinum pan, in which the previous concentration to 92.5 per cent. is effected, suffers very little indeed. The concentration in iron is not suitable below 95 per cent. or much above this point.

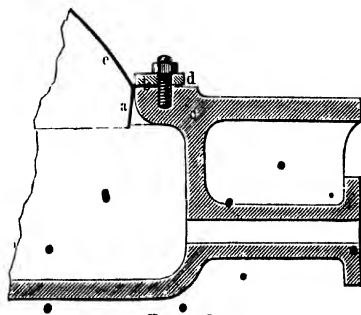


FIG. 438.

For this reason Scheurer-Kestner prefers the following combination of a cast-iron pan with platinum dome (Ger. P. 61331; *Bull. Soc. Ind. Mulhouse*, 1892, p. 320). Fig. 438, again, shows

the arrangement of protecting the iron from drops of weak acid by the platinum apron *a*, and of forming the joint by means of the platinum flange *b*, held between the iron flanges *c* and *d*. But here the platinum continues into a real hood, *e*, closed at top in the ordinary manner. The iron pan C, which weighs 250 kg., must be entirely surrounded by the fire, as shown in Fig. 439. The platinum dome weighs from 8 to 8.5 kg., and the preceding two platinum dishes B and A, provided with Faure and Kessler hoods, weigh 9 kg. each, the connection-tubes about 2 kg. The fire plays first under the weak platinum pan, then under the stronger platinum pan, at last under the iron pan. Such an apparatus furnishes 4½ tons of 95 per cent. acid in twenty-four hours, with less than 0.15 g. platinum lost for each ton of acid; and the concentration can be easily driven to 97.5 per cent.

Herreshoff, H. Nichols, and G. Nichols (B. P. 1998 of 1887; Amer. P. 357528) cause sulphuric acid, previously concentrated up to 86 per cent.  $\text{H}_2\text{SO}_4$ , to flow in a heated zigzag canal, whereby it is exposed to such a degree of heat that it is concentrated up to 95 or 96 per cent. From here it flows into another similarly shaped vessel, heated to such a degree that half or two-thirds of the acid goes away in the shape of vapour and is condensed in the shape of acid of 93.5 per cent., nearly chemically pure; the acid remaining behind contains about 98 per cent.  $\text{H}_2\text{SO}_4$ . Evidently this is the process referred to by Chandler (*J. Soc. Chem. Ind.*, 1908, p. 269), as follows. Herreshoff concentrates the acid coming from his tower (*suprà*, p. 867), first to 65° Bé. in platinum, then in an iron pan to over 66° Bé. While passing through this, most of the acid is distilled off and condensed in a platinum Liebig's condenser to 66° Bé.; this acid is free from arsenic and very pure. The acid which passes through the stills without distillation represents a small proportion of the total and has a strength of 98 per cent. At one single establishment 100 tons of distilled acid were made daily from pyrites, comparing favourably with the concentrated acid made from brimstone. (Chandler says in that place that in my treatise I state that the claims made by Mr Herreshoff for his still were impossible. There is some mistake about that; I nowhere made such a remark. I am informed from an

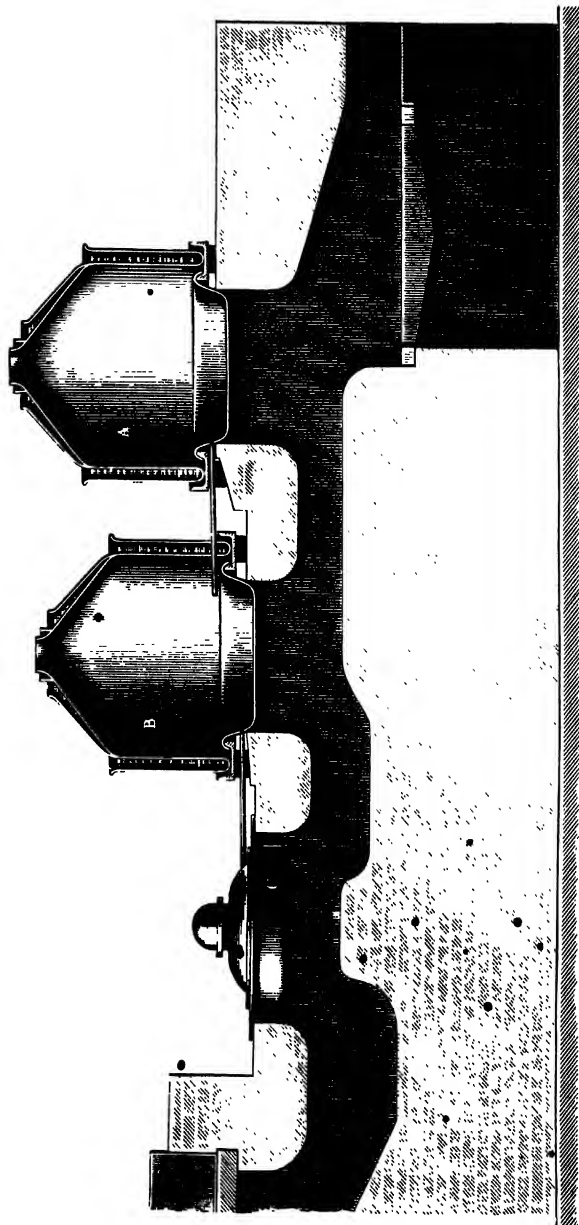


FIG. 439.

absolutely trustworthy source that the above-described process is still in successful operation.)

The Clayton Aniline Co. (B. P. 11544 of 1898) employs cast-iron pans in such a manner that the acid, of any desired strength, is run on to the centre of the surface of heated acid containing not below 90 or 93 per cent.  $H_2SO_4$ , at the same time withdrawing so much strong acid from the bottom of the vessel that the level remains nearly constant. This system is shown in Fig. 440. Pan *a* has an overflow pipe, *b*, starting near the bottom of the pan at *c* and delivering the acid at *d* at a suitable level. On flange *e* the cover *f* is fixed

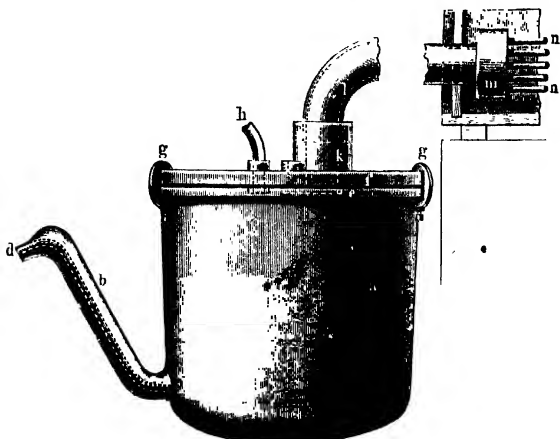


FIG. 440.

by screw-clamps, *g g*, with a suitable cement. Through neck *h* the fresh acid is introduced. In neck *k* a pipe, *l*, is fixed, through which the vapours escape, which are condensed by means of chamber *m* and cooling-pipes *n n*. Through another neck a thermometer is introduced into the pan. For a start pan *a* is charged with acid of 90 to 93 per cent. which is heated to boiling, whereupon fresh diluted acid is run into the pan in suitable proportions, striking the acid in *n* about the central part. The supply is regulated in such a manner that the level remains practically constant, the strong acid running off at *d* and the vapours escaping at *l*. (An altogether similar process is described in Gridley's Amer. P. 265495 of 1882.)

This apparatus has since been combined with another, intended to deal with the acid fumes, to be described below.

C. Krell, of Bruchhausen, near Küsten, in Westphalia, has constructed an apparatus, consisting of a cast-iron pipe heated in a bath of molten lead, the ends being water-cooled so that the solid lead forms a tight joint against the molten portion.

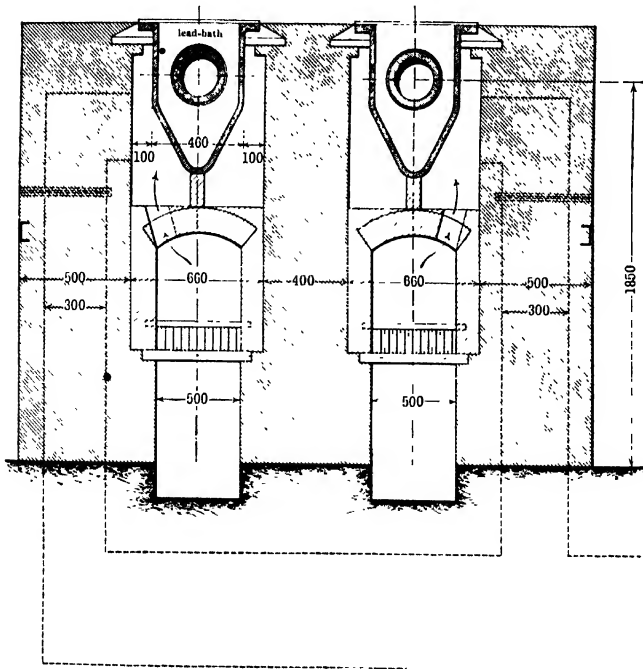
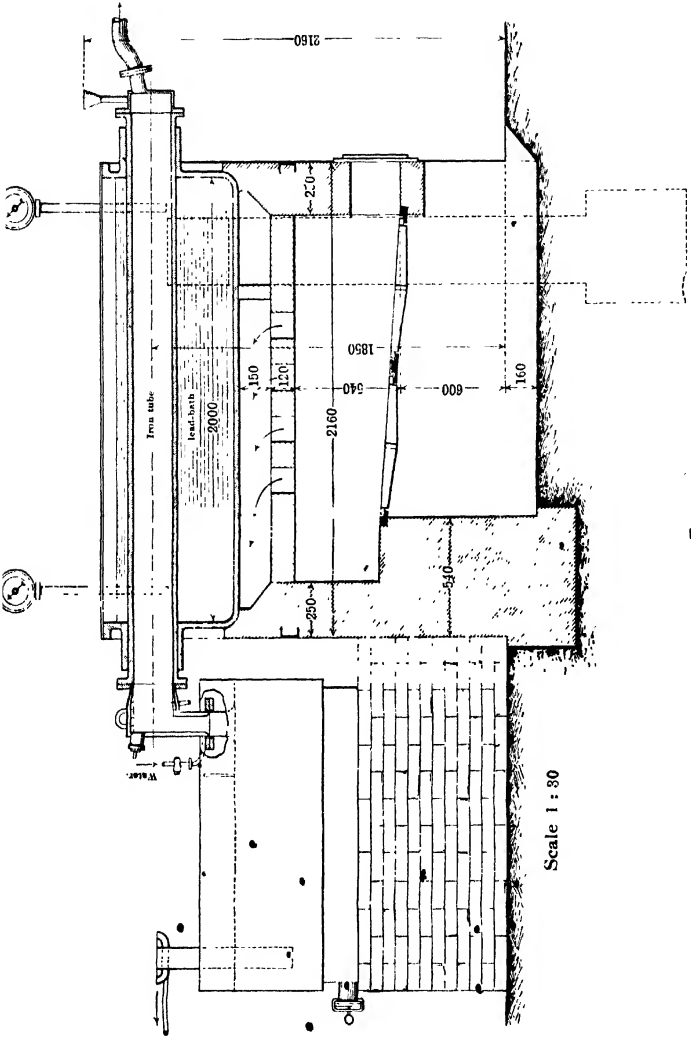


FIG. 441.

Figs. 441 to 443 show this system with all details (B. P. 18727 of 1894). One such pipe, costing £4 to £4, 10s., yields from 300 to 500 tons strong sulphuric acid, according to the strength of the feeding-acid, with one man per shift. The cleaning can be mostly performed without any stoppage of work; once a week, or in two or three weeks, a thorough cleaning must be effected, which involves a stoppage of half a shift. An apparatus for turning out 5 tons commercial O.V. (92 to 93 per cent.) requires





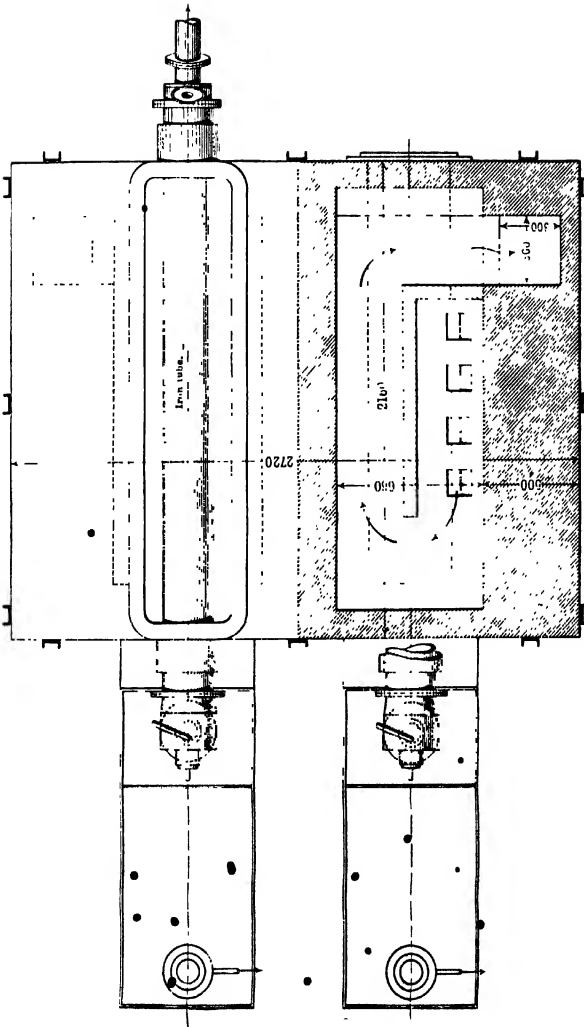


FIG. 443.

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a ground space of 120 sq. ft., including cooling-apparatus, and costs £150, or inclusive of all auxiliary apparatus, brickwork, etc., £250, to which must be added £250 for the licence, plans, and instructions. For acid of 97 per cent.  $H_2O_4$  iron pipes are employed at an additional cost of £100. This plan works very well for concentrating Glover acid or waste acids from nitroglycerine, etc. It has been at work for some years in several factories in Germany and Poland. M. Liebig (*Z. angew. Chem.*, 1900, p. 184) speaks very well of it.

Hartmann and Benker (*Z. angew. Chem.*, 1906, p. 565) admit the success of the Krell apparatus, with the remark that it is more suitable for regenerating waste acids from purifying processes than for producing commercial acids. Krell's Ger. P. 166557 describes arrangements for cleaning the pipes of his apparatus. His Ger. P. 176944 (B. P. 4063 of 1906; Fr. P. 363604) describes a combination of inside pipes made of chilled white cast-iron, in short pieces, surrounded by a jacket of ordinary cast-iron.

Stolzenwald (*Z. angew. Chem.*, 1910, p. 1977) states the cost of a Krell plant for producing 5 tons acid of 97 to 98 per cent. per diem, inclusive of previous concentration, at £750 to £800, inclusive of patent royalty; the consumption of coal for firing is  $1\frac{1}{2}$  tons per day.

A special plan was proposed by Hartmann (B. P. 2839 of 1879). The acid is to be saturated with iron salts, which are again separated on concentration, and are intended to protect the iron of the pan itself.

The following process is intended to combine concentration of sulphuric acid with purification from iron and arsenic. Menzies (B. P. 3230 of 1883) asserts that sulphuric acid of the highest concentration can contain but traces of iron and arsenic in solution, provided the latter be present as arsenic acid. He adds some nitric acid, in order to oxidise any  $As_2O_3$  to  $As_2O_5$ , and boils the acid in a cast-iron pan, the bottom of which is not exposed to the fire, until the strength of the acid distilling over is about  $142^\circ Tw$ . The fire is now drawn, the acid is allowed to settle, and two-thirds or three-fourths of the clear acid is withdrawn. This acid is colourless and free from Fe and As [ $?$ ], and 3 or 4 per cent. stronger than ordinary "rectified O.V." Fresh oxidised acid is run into that which

has remained in the pan, in such a way that the strength never falls below that at which the iron is acted upon by the acid. According to analyses quoted in the *20th Official Alkali Report* (for 1883), p. 45, the quantity of iron found in the concentrated acid, calculated as Fe, is only from 0.006 to 0.022 per cent.; that of As, 0.013 to 0.015 per cent.; that of  $N_2O_3$ , 0.011 to 0.024 per cent. The precipitate at the bottom of the still contains 50 per cent.  $SO_3$ , 20  $As_2O_3$ , 28.2  $Fe_2O_3$ , 1.8 insoluble, etc.

These figures\* show that the removal of arsenic by Menzies's process is nothing like complete. Menzies believes that acid of 58° Bé. does not act (in the heat) upon cast-iron; but that is a great mistake, and in practice he must have dissolved a large quantity of iron which no doubt in the latter stage of the process would be again separated in the shape of anhydrous ferric sulphate.

In the *28th Alkali Report*, p. 55, Graham's process is mentioned, in which the concentration takes place in a series of cast-iron dishes. It was found that hot sulphuric acid, in thin layers, in contact with cast-iron, tends to dissociate into  $SO_3$  and  $H_2O$ , so that from a certain point the acid becomes all the weaker the longer and more strongly it has been heated. The dissociation is evidently caused by the superheating of the iron, which becomes much hotter than the platinum.

[This observation proves the advantage, formerly pointed out by us, of causing the flame to travel in the same direction as the acid, so that the strongest acid is not in contact with the hottest part of the flame. In such dishes the acid cannot very well be got up higher than 92 or 93 per cent.  $H_2SO_4$ , whilst in deeper cast-iron pans higher strengths can be reached, and they cost so much less than most other apparatus, that even their short life (about one or two years) is of no consequence.]

Fisher, Hall, and Moore (B. P. 27376 of 1898) let the acid run through a long cast-iron pipe heated outside, to produce continuous concentration.

The *38th Alkali Report*, p. 18, mentions a process of American origin, by which sulphuric acid is rectified continuously in a cast-iron vessel, all air being excluded from the space above the liquid acid. In this case there is no difficulty in condensing all the  $SO_3$ ; very little  $SO_2$  is formed, and the gases escaping are not in the vesicular condition rendering

## 1174 THE CONCENTRATION OF SULPHURIC ACID

condensation so difficult and imperfect in other processes. The process had not been at work sufficiently long to test all these claims. According to Report No. 41, p. 134, a similar plant had been erected in a factory where it had given continual trouble, both in respect to yield and discharge of acid fumes. The condensing plant would have to be modified considerably to avoid nuisance.

P. Kestner (Ger. P. 121339) concentrates the acid by heating it in a perpendicular iron tube, in which it is raised to a higher level by the gas-bubbles. He also (Ger. P. 177304) concentrates the acid in perpendicular pipes, heated outside, without introducing air or gases into the liquid by forcing this into the pipes under a pressure not sufficient for driving it up to the upper part, and compelling it to rise in thin layers along the inside walls of the pipes through the formation of vapours. The B. P. is 12502 of 1906.

Those apparatus where cast-iron vessels are used in connection with a *vacuum* process will be mentioned later on.

Mackenzie's apparatus is described in *Chem. Trade J.*, 1905, xxxvi. p. 160. Acid of sp. gr. 1.55 is run from a store tank through a lead coil, heated by the waste gases from a tower below, filled with bricks, where it is concentrated to sp. gr. 1.775 to 1.80 by direct contact with the hot fire-gases, coming from the cast-iron pot, where the final concentration takes place. Here hot air, produced in a chamber containing cast-iron pipes, is blown through, while the pot is externally heated by the gases coming from the air-heating chamber. The temperature in the cast-iron pot need not exceed 270°, since the hot air blown through is sufficient to bring up the acid to full strength at that temperature. This system is patented as B. P. 26278 of 1904.

Ellison (B. P. 17760 of 1902) concentrates sulphuric acid in a closed cast-iron pan, within which is a pipe of acid-resisting material, of rather less diameter than the pan, and having its bottom edge serrated. Dilute acid is led into that pipe and is concentrated by the heat from the surrounding strong acid. As the acid in the inner pipe becomes concentrated, it flows through the serrations to replace the concentrated acid in the pan. A leading object of the invention is that only concentrated acid shall come into contact with the cast-iron boiler.

Evers (Ger. P. 176369) effects a continuous concentration of acids by means of two coils of pipes, interposed between each other, on the bottom of the pan, through which the liquid passes on. The concentrated acid runs out at the side, after having given up part of its heat to the dilute acid introduced in the centre of the vessel.

Stange (B. P. 91 of 1907; Ger. P. 188901; Amer. P. 837592; Fr. P. 372326) concentrates sulphuric acid in conical cast-iron pans, the sides of which are heated outside, by means of hot air being blown over the surface of the liquid. The bottom of the pan is cooled, so that the precipitate does not burn fast, and has a conduit communicating with a cooling-chamber beneath. In the pan a stoneware vessel with an opening at the bottom is suspended, through which the dilute acid must pass before getting into the cast-iron pan. Thus the lighter, dilute acid floats on the already concentrated acid, which does not mix with it, as it is prevented from boiling by the cooling of the pan-bottom. Therefore the sludge inevitably formed when concentrating sulphuric acid in cast-iron vessels does not burn fast to the bottom, but remains in the form of a mud, which is easily let out at the bottom without stopping up the outlet for the concentrated acid situated higher up. The escaping vapours are condensed in a Glover tower.

Proelss and Hall (Amer. P. 960702) employ a cast-iron pot or boiler, provided on the top with an annular flange and rim; from this a pipe leads to an extension with interstitial "packing" over which the weak acid flows on its way to the boiler. As the level of the acid boiling in the pot rises above the flange, the strongest acid from the bottom passes out and upwards by a tube into a second pot placed over the first; here the acid is made to travel over the bottom in a thin layer, and is thus highly concentrated. Acid of 98.2 per cent. is said to be continuously produced by this apparatus.

Friedrich (*Chem. Zeit.*, 1909, p. 478) recommends that kind of cast-iron concentrating apparatus in which acid of 60° or 50° B $\acute{e}$ . is run on to the surface of a large quantity of boiling acid of 60°, and the concentrated acid is continuously run out at the bottom by means of a syphon (a fixed tube from the bottom, with an overflow at the top, is quickly stopped up by mud). He proposes, instead of this, to connect the bottom of

the vessel with an acid-egg, serving as a mud-collector, and, later on (*ibid.*, p. 634), to pass the vapours escaping from the pan through a small tower like a Glover tower, fed with chamber-acid to such an extent that the gases issuing from it have a temperature of about 100°.

Gellen (Austr. P. appl. 5616) employs a cast-iron apparatus, consisting of a cascade of dishes, through which the acid runs down and is exposed to the hot acid gases coming from a previous concentration.

Hartmann and Benker (*Z. angew. Chem.*, 1909, pp. 395-7) later on carry out the "Benker" system, described *suprà*, p. 1121, by means of a combination of lead and cast-iron vessels. According to them, although there are several other competing systems, the "Benker" plan keeps a permanent place, since several great improvements of it have been made, and it is so cheap to erect and to work, with very little distilling acid. The eight lead pans employed for the first concentration are now arranged in two sets of four each, heated by the waste fire of the cascades. The pans are made of a special acid-resisting description of lead ("Krellblei"), which is not exposed to the sudden destruction observed by Lunge and Schmid (*suprà*, p. 325), even on boiling acid of 98 per cent., *i.e.* at temperatures of 320°, so that the acid can be brought up in them to 63° Bé. without any considerable wear and tear. For the cascade itself they have given up the application of porcelain dishes, which were subject to pretty frequent cracking; they now employ cast-iron dishes, made of the so-called "neutral iron" by the A. G. für Bergbau und Eisenhüttenbetrieb at Kattowitz (Silesia), which is the best acid-resisting cast-iron as yet at the disposal of chemical factories. These dishes are now made 320 mm. wide at the top and 165 mm. deep; they are placed on fire-clay rings, *not* on such dishes as had to be done with porcelain capsules, and are fired directly. From these neutral-iron dishes the acid comes out water-white, and not distinguishable from acid concentrated in platinum. Also the quartz-glass dishes of the Thermal Syndicate, Newcastle (p. 1123), have stood very well. From October 1907 to January 1909 the firm has supplied 1200 "neutral-iron" dishes and 300 "quartz-glass" dishes, without having had any complaints about them from their customers. (The neutral iron is also very useful for the

concentration of nitric acid.) They have also greatly improved the way of heating the cascades, by the introduction of step-grates, and have made several other improvements, of the acid coolers, the roof of the Volvic flues, etc. Of the far above 100 plants erected according to their system in all countries, about 20 serve for the recovery of pure acid from waste acid of the industries of explosives, coal-tar colours, petroleum refining, etc., etc., without a single complaint having been made on the durability of the plant and the quality of the acid made therein.

Figs. 444 to 446 show the last construction of the Benker apparatus (1911). Two parallel rows, *a, a*, of comparatively thin plane plates of acid-proof "neutral" cast-iron are arranged in cascade form, so that the acid runs down upon them. The plates rest on the sides of the fire-flue *c*, conveying the gases from a common coke-gas producer, *d*. Owing to the greater fire-surface and the thinner layer of acid on the plates, the evaporating-action is much stronger than in cast-iron or quartz dishes. The vapours from the cascades are drawn off separately for each, by a Kestner fan, *e*, into a cooler, *f*; in case of repairs or exchange of plates, each cascade can be worked by itself, without interruption of work. The fire-gases on leaving the cascades are now (in lieu of the formerly employed lead pans) utilised in a Volvic-lava tower, *g*, packed in the usual way and fed with chamber or Glover acid by the distributor, *h*; the acid arrives at the bottom, 61° or 62° B $\acute{e}$ . strong, and through neutral-iron pipes, *i*, goes to the principal concentrations. The fan draws through *k* the acid vapours from the tower, through a lead-cooler, *l*, and ultimately through a coke-filter, *m*, which retains the last traces of acid. The distilling-acid shows 20° to 35° B $\acute{e}$ ., and can be reconcentrated together with the chamber-acid. The concentrated acid shows up to 98 per cent. N $_2$ SO $_4$ , and is as clear as water. The cleaning holes *n, n* in the acid channel allow its being cleaned out. This system furnishes per diem 9 to 10 tons acid of 92 to 93 per cent. H $_2$ SO $_4$ , with a consumption of 12° to 14 per cent. coke, or 5½ to 6 tons acid of 97 to 98 per cent. H $_2$ SO $_4$  with 22 per cent. coke, and costs about £650. The loss of acid is 2 or 3 per cent. when going up to 93 per cent., and correspondingly more when going higher up.



FIG. 444.

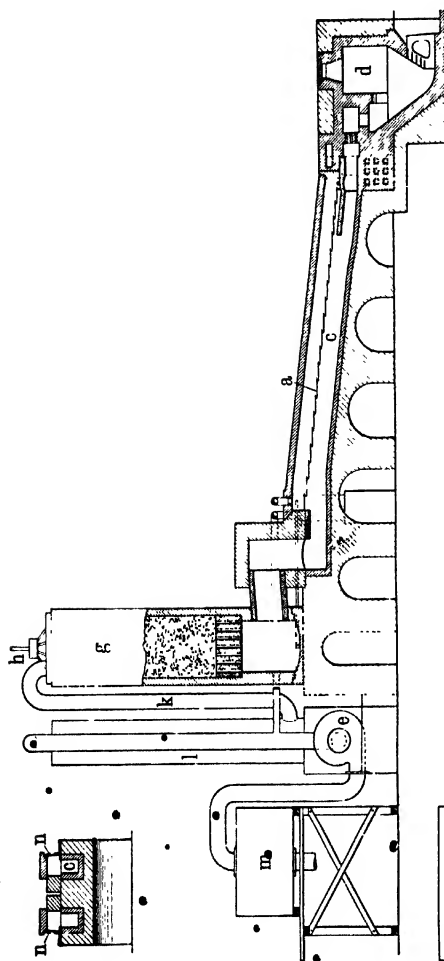


FIG. 446.

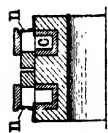
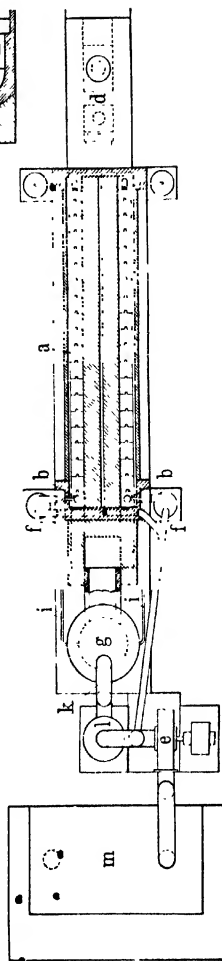


FIG. 445.



*Ferro-silicium*, containing a large proportion of silicium, as manufactured by the process of Jouve and sold by the name of "melliture," resists the attack of all acids except hydrogen fluoride, and can be employed for casting pans in which sulphuric acid is to be concentrated, as pointed out by J. Hoffmann in *Chem. Ind.*, 1911, p. 241. A similar material, sold by the name of "tantiron," is stated in *Chem. Zeit.*, 1911, p. 1067, to be used in England for that purpose (p. 1129).

*Concentration of Sulphuric Acid in Wrought-iron Vessels.*

Tate (*J. Soc. Chem. Ind.*, 1894, p. 208) gives particulars of an old tar-still, made of  $\frac{3}{8}$ -inch plate, 6 ft. wide and 4 ft. high, in which for several years past a mixture of sulphuric and nitric acid had been concentrated from sp. gr. 1.75 to 1.838, with recovery of the nitric acid. [Perhaps the use to which this vessel had previously been applied had deposited a protective, carbonaceous coating.]

*Recovery of Sulphuric Acid from Waste Acids (Acid-tar, Sludge-acid) of Nitrating Processes.*<sup>1</sup>

For this purpose nearly always iron pans, usually preceded by lead pans, are employed, as such dirty acids generally form crusts which speedily destroy platinum pans. The unavoidable contamination of the acid with iron is also no great drawback in this case, as the recovered acid is again used for the treatment of mineral oils, etc. We have already touched upon this *suprà*, pp. 1075 and 1164.

The following process serves for the concentration of acid recovered from the "acid-tar" or "sludge-acid" of petroleum refineries. This acid-tar is first diluted with water, whereupon most of the tar is separated and skimmed off (Amer. P. of Fales, 97182 of 1867). The acid liquor is now concentrated in leaden pans, first by bottom heat and then by top heat, up to a

<sup>1</sup> The recovery of nitric acid from waste-acid mixtures has been already described on p. 197.

strength of 64° Baumé (American hydrometer). The last concentration takes place in cast-iron pans with leaden hoods. The pans, two of which work together terrace-wise, are 2 × 4 ft. wide and 6 ins. deep; they have a rim shaped for a hydraulic lute, lined with lead, into which dips a double-walled, roof-shaped, leaden hood, through which water is kept running, on the principle of Faure and Kessler's stills (pp. 1142 *et seq.*). All the joints are made with asbestos cement. The principle of this apparatus is shown in the sketch, Fig. 447.\*

Ostrejko (*Chem. Zeit.*, 1902, *Report*, p. 360) describes the recovery of sulphuric acid from acid-tar by the well-known process of diluting to 32° BÉ., separating the tar, and concentrating to 60° BÉ. In order to complete the separation, the

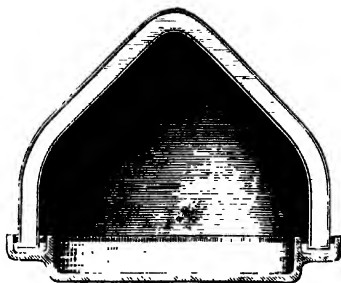


FIG. 447.

acid is again diluted with chamber-acid or water and boiled down. The removal of the tar is promoted by adding a certain description of carbon invented by the author of that communication; 1 per cent. of this is said to convert the acid into a colourless product.

U. Wedge (*J. Soc. Chem. Ind.*, 1899, p. 345) describes the usual process of working up the "sludge-acid" from the petroleum refineries. As it comes from these it contains about 45 per cent. of oil. Most of this is separated by diluting the acid to 35° BÉ.; it is called "acid-oil" and is utilised as fuel. The weak acid separated from it still contains 1.2 per cent. oil. It is heated in a shallow, hooded lead pan by means of a light steam-coil to 110° C., in which process a very slight quantity of sulphur dioxide is formed. The acid now enters a series of three shallow lead pans, 6 × 45 ft., 12 in. deep,

covered with brick arches, where it is treated with surface-fire ("weak-acid pans"). Here it gets up to  $55^{\circ}$  Bé. and a temperature of  $166^{\circ}$  C., with some loss of  $\text{SO}_2$  and  $\text{SO}_3$  (the gases showed 1.24 grains  $\text{SO}_2$  and 0.92 grain  $\text{SO}_3$  per cubic foot). Now the acid enters a series of two lead pans of the same size as the above, and at last two iron pans  $3 \times 7$  ft., 9 in. deep. The lead pans are also housed in brick and heated by surface-fire. From these ("strong-acid pans") the acid issues with a temperature of  $230^{\circ}$  C., and shows  $66^{\circ}$  Bé. =  $92\frac{1}{2}$  per cent. acidity. The gases from these pans showed 28.7 grains  $\text{SO}_2$  and 4.9 grains  $\text{SO}_3$  per cubic foot. There was a total loss of 25 per cent. of the acid, 91 per cent. of which occurs in concentrating from  $56^{\circ}$  to  $66^{\circ}$  Bé., 86 per cent. being caused by the action of the oil on the sulphuric acid forming sulphur dioxide, which cannot be recovered in consequence of the heating by surface-firing. Calculation shows that 1 lb. of the hydrocarbon dissolved in the oil will destroy 20.88 lbs. acid of  $92\frac{1}{2}$  per cent.

The treatment of sludge-acids in iron vacuum-retorts will be described later on.

Hartmann (*Chem. Zeit.*, 1899, p. 147) concentrates waste acid from nitrating processes up to  $61^{\circ}$  Bé. (sp. gr. 1.732) in six lead pans. The acid, at a temperature of  $145^{\circ}$  or  $150^{\circ}$ , then passes through a small "preliminary" cast iron pan, provided with a leaden hood and a chimney for carrying away the vapours, which contain very little acid. Now  $180^{\circ}$  hot, and of sp. gr. 1.785 to 1.796, it runs into two cast-iron pans with cast-iron covers, one placed higher than the other, and runs away at a strength of 97 or 98 per cent.  $\text{H}_2\text{SO}_4$ . Each of the latter has its own fire, as well as the "preliminary" pan, the waste heat of all heating the lead pans. For the production of  $5\frac{1}{2}$  to 6 tons strong acid in twenty-four hours, the preliminary pan weighs about 24 cwt., the two covered pans with appurtenances about  $7\frac{1}{2}$  tons. The consumption of coal is 20 per cent. The small pan lasts three or four months: the upper one of the large pans six to nine months, the lower one twelve months or more. The castings should be made of hard metal and without flaws, and the two large pans must be entirely surrounded by the fire. The wear and tear of these castings represent 2s. per ton of strong acid. The cost of the whole plant, including all

auxiliary apparatus, is about £750. It should be mentioned that *platinum* retorts would suffer enormously if waste acid was to be brought up to 97 or 98 per cent.

Benker has applied his porcelain apparatus (p. 1121) also to the recovery of waste acids. In the case of acid tar from refining petroleum there is a loss of about 40 per cent.; the acid is coloured black, owing to the formation of graphite, but furnishes water-white petroleum. The recovered acids from nitroglycerine or nitrocellulose are yellowish, but perfectly fit for being used over again.

Waring and Breckenbridge (Amer. P. 643578 of 1900) purify sludge-acid by heating with about 4 per cent. sodium nitrate at a temperature of 15° to 82° C.; 1 per cent.  $\text{NaNO}_3$  suffices for removing offensive odours.

Friedland and Ljubobarski (Rus. P. 6631) dilute the acid-tar, skim off the tar, allow to settle, and submit the clear liquid, brought to 50° Bé., to the electric current, which oxidises the carbonaceous matter to  $\text{CO}_2$ .

Fleischer (Ger. P. 182246) puts the acid-tar in porous earthenware vessels, which are placed in water; pure sulphuric acid diffuses through the earthenware into the water, and the tarry substances accumulate inside the vessel, up to a maximum. The water outside is ultimately converted into acid of about 1.52 sp. gr.

Blacher and Sztencel (Amer. P. 956276) obtain pure acid from the sludge-acid of petroleum refineries by running it into boiling concentrated sulphuric acid, blowing air through this and condensing the escaping vapours (*cf.* p. 1184, the report of Wispek on the patents of the Steaua Romana Petroleum Company).

Stolzenwald (Ger. Ps. 212000 and 213589; Austr. P. 42408; *cf.* also his statements in *Chem. Zeit.*, 1908, p. 1017) introduces the waste acids, of whatever origin, in the crude state, or diluted with water, of preheated, at the bottom of upright, annular boiling-pipes, provided at the top with outlets for gases, and for the concentrated acid, and arranged in such manner that the temperature gradually increases from the bottom upwards. In the lower, cooler part of the pipe the oily matters are separated by the effect of concentration; in the hotter, upper part of the pipe the resins and tars and a little of the sulphuric

acid are decomposed. The final products are oils, sulphuric acid,  $\text{SO}_2$ , and carbon. The latter is carried along by the acid, and is separated from this by subsidence or filtration. The gasified oils and the  $\text{SO}_2$  escaping at the top are separated by cooling, and the  $\text{SO}_2$  can be worked for sulphuric acid. Before passing the waste acid through this apparatus, it may, after treating it with water and preheating, be treated in such manner that the escaping oils are recovered by cooling, while the resins and tars are separated on the surface of the acid as a solid paste, leaving behind a sulphuric acid of about  $50^\circ \text{Bé}$ .

Donath (*Chem. Zeit.*, 1904, p. 1153) describes the very well-known plan of utilising waste sulphuric acid (from petroleum refining, etc.) by heating to about  $300^\circ$  with nitrogenous substances, such as leather, hair, etc.; by extracting the product with water, ammonium sulphate is obtained, and the residue may be utilised for decolorising purposes, or for producing potassium ferrocyanide.

Wispek (*Petroleum*, June 1911, pp. 1045-48) discusses the utilisation of the waste acids from the refining of petroleum. Two classes of such "acid-tars" must be distinguished, viz., those produced in the refining of petroleum-naphtha ("benzin") and lighting oil, and those from the refining of lubricating oils. In refining benzin or petroleum, about 10 per cent. of the sulphuric acid are decomposed, and 90 per cent. remains behind, mixed with so much organic substance that for each 100 parts fresh acid of  $66^\circ \text{Bé}$ , used in the refining process, 125 to 130 parts waste acid of  $50^\circ$  to  $55^\circ \text{Bé}$  are formed. By diluting this with water to about  $35^\circ \text{Bé}$ , most of the organic substance (say 20 to 25 per cent. of the waste acid) is separated in the form of a black, repugnantly smelling tar, sp. gr. about 0.900, boiling principally between  $100^\circ$  and  $200^\circ$ , and containing about one-third neutral oils and two-thirds compounds of an acid nature. The whole of the sulphuric acid collects at the bottom in the form of brown, clear, dilute acid, which must be concentrated. In the waste acid from refining lubricating oils, the proportion of sulphuric acid is about 80 per cent.; it is even in the warm state a thick liquid, from which the resinous matters are not easily separated. This acid-tar is partly freed from sulphuric acid by heating in large cast-iron pans by means of direct steam, sometimes also by a coal-fire from below,

so that part of the sulphuric acid is driven out; the tarry matter remaining behind is burnt under the oil-pans. The recovery of *pure* sulphuric acid of 66° Bé. from these acid-tars has not been until recently successfully accomplished, in spite of many attempts; the acid obtained was always black and always retained injurious organic compounds. According to the process of Pilat, Bolland, and Selcer (Austr. P. 31595 of 1907), or Julius Fleischer (Ger. P. 182246, *suprà*, p. 1182), it is indeed possible to obtain a water-white, dilute sulphuric acid, free from tar, by submitting the acid-tar to diffusion with water through a porous diaphragm. But that white, dilute acid contains all the organic and sulphoacids, which on concentration decompose and again stain the acid black. No more successful, according to Wispek, seems to be the process of Stolzenwald (*suprà*, p. 1182).

Pfeifer and Fleischer (Austr. P. 43739 of 1910) treat the acid-tar with silico-compounds; but the yellow acid obtained thus turns black on concentration. The same takes place when filtering the acid through bone-charcoal, or when heating it with nitric acid, and moreover these processes are too costly. The widest application has been secured by the process of Hartmann and Benker (continuous concentration in lead pans up to 60° Bé., and then in cascades of porcelain dishes to 66° Bé.), *suprà*, p. 1122, but this proceeding, according to Wispek, is very troublesome; there is much SO<sub>2</sub> given off, and so much carbonaceous and asphalt-like substance is secreted that the overflows are stopped up and have to be constantly made free by perforating these crusts, and the concentrated acid is also black. But by the process of the Steaua Romana Petroleum Co. (Austr. P. 42293 of 1910; Ger. Ps. 221613 and 224566; patented in the U.S. America by Blacher and Sztencel, *cf.* p. 1182), 75 to 80 per cent. of the sulphuric acid originally employed are recovered in the form of pure white acid of 97 to 98 per cent. The said Company at Campina (Roumania), where 150 cisterns of crude petroleum, at 10 tons each, are worked up, and where they produce their own sulphuric and fuming acid by the Tentelew contact process (Chap. XI.), yielding every day more than a truck-load of acid-tar, in 1907. introduced the new process, consisting in heating strong pure sulphuric acid in a retort to boiling, and continuously running in black acid, either as such or as it is obtained from acid-tar by dilution, together with passing through

acid are decomposed. The final products are oils, sulphuric acid,  $\text{SO}_2$ , and carbon. The latter is carried along by the acid, and is separated from this by subsidence or filtration. The gasified oils and the  $\text{SO}_2$  escaping at the top are separated by cooling, and the  $\text{SO}_2$  can be worked for sulphuric acid. Before passing the waste acid through this apparatus, it may, after treating it with water and preheating, be treated in such manner that the escaping oils are recovered by cooling, while the resins and tars are separated on the surface of the acid as a solid paste, leaving behind a sulphuric acid of about  $50^\circ \text{Bé}$ .

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Messrs Blacher and Sztencel must be acknowledged to have completely solved the difficult task of dealing with that troublesome waste product.

E. B. Gray (Amer. P. 1005425) concentrates weak acid derived from petroleum sludge by a series of intercommunicating open pans, followed by a series of stills, also intercommunicating, each provided with a water-jacketed head and condenser. The stills and pans are all placed in the same level on the furnace, the liquid from the last pan discharging into the first still.

C. L. Robinson (Amer. P. 1014520, assigned to the Standard Oil Co.) heats the acid sludge in a still to above  $500^{\circ}$  F. ( $260^{\circ}$  C.), whereby it is decomposed and a mixture of  $\text{SO}_2$  and hydrocarbon vapours is given off. This is passed through a condenser where the less volatile hydrocarbons are separated and the gaseous portion is then passed through a sulphur burner and forward to a sulphuric acid plant.

*Cast-iron Pans protected by Enamel or otherwise.*

It might be thought that *enamelled* cast-iron would be more suitable for the concentration of sulphuric acid than ordinary cast-iron. In fact, Roder (*Dingl. polyt. J.*, cxi., p. 397) proposed enamelled cast-iron boilers, and indicated a special kind of enamel for them: 1 part of powdered burnt alum, 4 parts of red-lead, and 2 parts of pure silica are to be melted together; the fluxed mass is to be cooled in water, dried, powdered, and 15 parts of it intimately mixed with 20 parts of pure silica and 3 parts of tin oxide. The whole is ground up with spirit of turpentine, laid with a soft hair-brush on the smoothly turned inner surface of the boiler; and this is repeated three or four times, each coat being allowed to dry first. The enamel is then fixed by fusing on as usual. But even the best enamel will resist only a very short time the boiling sulphuric acid and the uneven expansion and contraction of metal and enamel at the very greatly differing temperatures which occur in that process, and his proposal has had no practical success.

Wolters (Ger. P. 15639) states that by heating a mixture of alkaline pyrosulphate with concentrated sulphuric acid in iron vessels, a crust of iron sulphide is formed which protects

the iron during distillation, so long as the pyrosulphate is left in the vessel.

Tate (*J. Soc. Chem. Ind.*, 1894, p. 208) mentions an apparatus constructed by West in 1883 on the continuous system, with an enamel or porcelain lining; nothing is known as to its success.

Dyson (B. Ps. 17699 of 1893 and 27769 of 1896) has made a cascade-apparatus, consisting of iron pans lined with a special enamel, connected by U-shaped siphons, which carry the acid from the bottom of each vessel into the upper part of the next. A set of eighteen pans produces 21 tons of strong acid per week. This apparatus is stated to cost £250, and to require 6 cwt. of coke per ton of acid. Some more details are given in *Chem. Trade J.*, xvii, p. 339. Chamber-acid of 100° Tw. is employed, and 100 tons acid of 168° Tw. is produced in one apparatus in forty-three days, with a consumption of 23½ tons of gas-coke; the wages are £19, 9s. 7d., or 3s. 10½d. per ton, which would be greatly reduced if the same men could look after two plants. In 1902 several plants on this system were in operation in England.

Seckendorff (*Wagner's Jahresh.*, 1855, p. 56) proposed to concentrate the acid in flat-bottomed iron retorts completely surrounded by fire. The retorts are to be filled with lead sulphate, sand, or gypsum; chamber-acid is to be run in till a paste is formed, and the retorts are then to be heated. The watery vapour first appearing is conducted into the chambers; the concentrated acid coming after this is to be collected in glass or stoneware vessels, and is said to be very pure, free from iron, and as concentrated as that from platinum; nor is the iron retort said to be acted upon very strongly. Probably this plan has never been actually tried at all.

J. Grindley (Amer. P. 265495) recommends cast-iron pans, protected at the top by an asbestos cement against the action of the acid. The pan is filled up to the proper level with acid of 66° Bé., and is fed in such a manner that the concentration never sinks below 65° Bé., in which case the pan is not acted upon. [This strength, equal to less than 90 per cent.  $H_2SO_4$ , is much too low to prevent action on the iron. The corresponding English patent, No. 4709 of 1882, has not been proceeded with.]

Flanagan (B. P. 3530 of 1901) employs enamelled cast-iron

pans, with water-cooled leaden hoods, placed at different elevations. There seems to be no new principle whatever in this invention.

A special kind of cast-iron, extremely fit for resisting the action of sulphuric and nitric acid, is made by the "Ferrum" Company at Zawodzie, under the name of "Neutraleisen" (neutral iron); *cf. supra*, p. 1177.

The Chemische Fabrik List, E. de Haen (Ger. P. 197074), produces acid-proof vessels, apparatus, and electrodes by pressing *tantalum* hydride into moulds and converting the moulded pieces into tantalum metal by heating them gradually, ultimately for two hours to a white heat, and slowly cooling. The hydrogen given off is first removed by a water air-pump, and later on by a mercurial air-pump, and with as good a vacuum as possible.

*Concentration of Sulphuric Acid by Cold or Hot Gases.*

Stoddart (*Chem. News*, xxiii. p. 167) proposed to force a current of cold air into sulphuric acid heated in a lead pan; acid of 140° Tw. is stated to be obtainable in this way if the temperature be 150° C., and the strongest oil of vitriol at a temperature of 260° C. This plan, if ever carried out on a large scale, was no doubt very soon given up again. There is no reason why a current of cold air should not do more harm by cooling the acid than it can do good by carrying away the vapour more quickly, the latter being done much better by top fire, where there is also no danger of splashing. It is well known that lead pans would not very long stand a temperature of 260° C.

Galletly (*Chem. News*, xxiv. p. 106), who had applied the same principle independently of Stoddart, only worked on a laboratory scale; he admits that on a large scale the process did not succeed; nor need we wonder at this, since both he and Stoddart applied cold air.

Success in this direction could only be expected from the application of hot air, which seems to have been first tried by Gossage in 1850.

Gossage's apparatus is fully described and illustrated in our second edition, pp. 735 *et seq.* It consists of a double-shelled lead tower, with an air-space between the two shells; the tower

the iron during distillation, so long as the pyrosulphate is left in the vessel.

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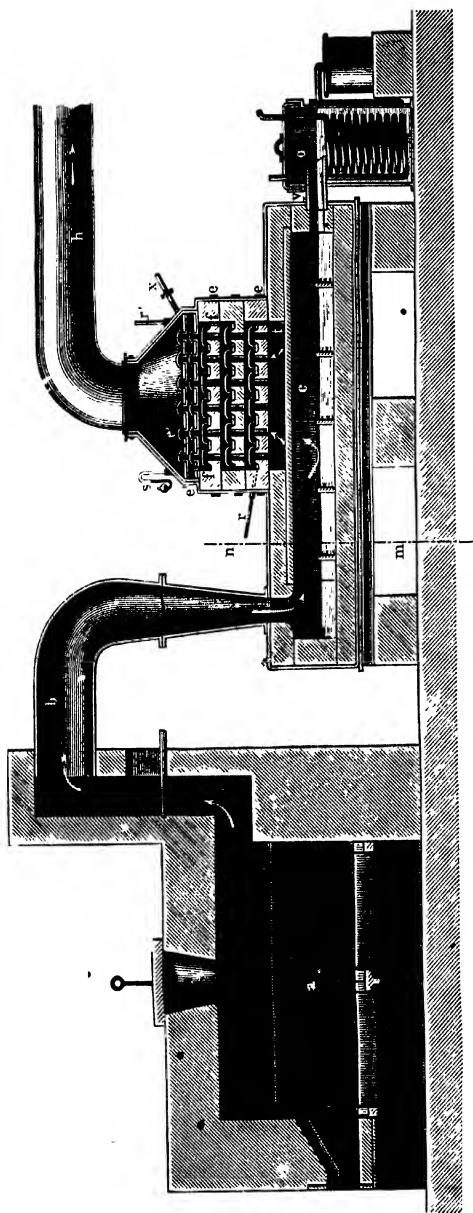


FIG. 448.

sulphuric acid; the vapours pass in a zigzag manner over several plates, over which fresh acid is running down. [It is not stated what material the vessel is to consist of.]

Gridley (Amer. P. 240248) applies strong heat to the under-surface of a thin body of dilute acid, and at the same time a blast of superheated steam or hot air to the upper surface, removing the vapours as they rise.

Falding (B. P. 17602 of 1893; Amer. P. 541041) constructs the pyrites-kilns, with hollow walls, by which the air passing through is heated, and can at will be introduced below the grates (*cf.* p. 436). The hot burner-gases are used for concentrating sulphuric acid, by passing them first into a small tower, consisting of specially acid- and heat-proof material (*viz.* Volvic lava of best quality), surrounded by a somewhat distant lead shell and packed with quartz. This tower is placed between the burners and the Glover tower, and receives the acid coming from the latter, which is here concentrated to 66° B $\acute{e}$ . The gases pass first into this intermediate tower, then into the Glover tower. Of course this acid is not pure. For pure acid the concentration in the first tower is brought only to 71.08 per cent. SO<sub>3</sub>; it is then run through a platinum tube into iron stills, as shown, p. 1159, where very pure acid up to 76.33 per cent. SO<sub>3</sub> distils over, while impure acid of 79.18 to 80.00 per cent. SO<sub>3</sub> (97 to 98 per cent. H<sub>2</sub>SO<sub>4</sub>) remains in the still, together with a mud of ferric sulphate and arsenic.—Falding thus applies the Glover tower to concentrate sulphuric acid to higher strengths than is done in the ordinary Glover tower, by constructing it with special care; but although he succeeded in getting acid up to about 90 per cent. H<sub>2</sub>SO<sub>4</sub>, his plan has not found much application (*cf.* Quinan's plan, *infra*, p. 1205).

The only hot-air process which has been thoroughly worked out, and has been introduced in many factories, is that of L. Kessler (B. Ps. 19215 of 1891 and 26169 of 1898). I am indebted for the following particulars, as well as the drawings, Figs. 448 to 450 (pp. 1190, 1192) to the inventor, and I have myself seen the process in operation at Clermont-Ferrand and in several other places.

The task in question requires several conditions to be fulfilled. The current of hot air must be brought into contact

## 1192 THE CONCENTRATION OF SULPHURIC ACID

with a sufficiently large surface of liquid to immediately reduce its temperature to a great extent. The air must thus

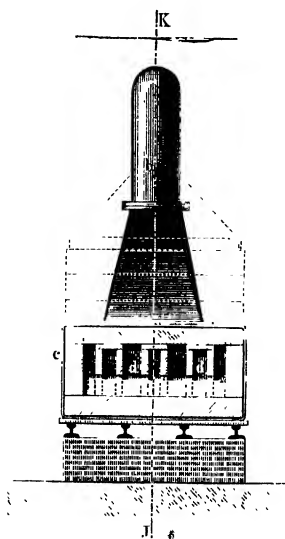


FIG. 449.

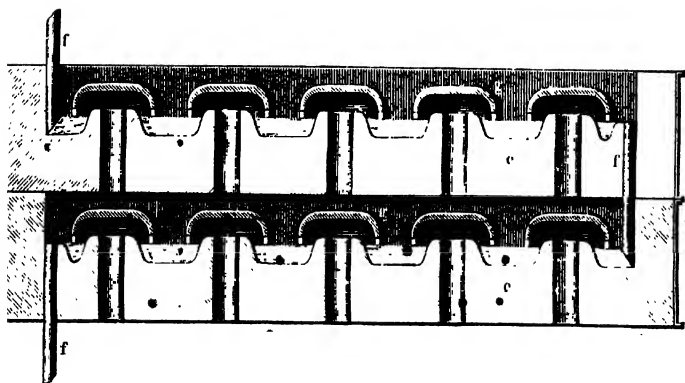


FIG. 450.

become completely saturated with steam and acid-vapour. The apparatus must not merely resist the action of the hot

air and hot acid, but it must be constructed in such a manner that the inevitably formed deposits and crusts do not give any trouble. Under these circumstances the acid can be concentrated far below its boiling-point. In order to produce acid of 95 per cent., boiling at  $284^{\circ}\text{C}$ ., the temperature need not exceed  $170^{\circ}$  or  $180^{\circ}$ ; for the most highly concentrated acid, boiling at  $320^{\circ}$ ,  $200^{\circ}$  to  $230^{\circ}$  is sufficient.

In order to denote both functions of this part of the apparatus visible at *c*, Kessler calls it a "saturex," because it saturates the fire-gases with acid-vapours, and it quenches the greatest part of their heat. The gases enter the "saturex" at  $300^{\circ}$  to  $450^{\circ}\text{C}$ ., and leave it at  $150^{\circ}$ . The acid-vapour contained therein is kept back in the "recuperator" mounted above the "saturex." This part of the apparatus exactly resembles the dephlegmating columns employed in the rectification of spirit of wine. It is fed with chamber-acid, previously employed for cooling the hot, strong acid issuing from the "saturex." This acid is divided over the numerous holes of the top plate, and gradually descends on to the four lower plates of the recuperator. In doing so it meets the hot air and vapour issuing from the saturex, and drawn through the liquid acid by applying suction at the end. In the recuperator the temperature sinks to  $85^{\circ}\text{C}$ .: this causes nearly the whole of the acid-vapour to condense, while the steam is not condensed, nor is there much fresh steam formed here. This is important, since any concentration of the acid in this place would cause deposits which would soon obstruct the holes in the plates.

Although the gases escaping from the recuperator contain next to no real *acid-vapour*, they contain some acid in the shape of *mist*, as well as some vapour of sulphuric anhydride. This mist is retained by two boxes filled with dry coke in pieces about the size of a pea (cf. *infra*, p. 1195); a little water condensing here converts the  $\text{SO}_3$  into  $\text{SO}_4\text{H}_2$ . The weak acid thus formed may be passed through the recuperator. The gases now issue into the air, moderately warm and perfectly free from acid, but charged with all the steam driven out of the chamber-acid. The distilling acid is thus completely condensed without the necessity of employing any cooling-water.

Figs. 448 and 449 show the apparatus. Fig. 448 is a



longitudinal section through line J K; Fig. 449 a cross section through the "saturex" according to line *m n*; Fig. 450 an enlarged section through some of the plates of the "recuperator." *a* is the fireplace, here shown as a simple grating, but in reality a gas-producer, with gas-coke as fuel. The fire-gases pass through a cast-iron pipe, *b*, flattened below so as to cover the whole breadth of the satorex *c*. This is a trough, composed of acid-proof stone slabs, surrounded by a thick lead jacket and placed upon an open foundation. The stone must resist hot acid and hot gases, e.g. Volvic lava; but even if it were somewhat porous, the lead jacket would retain any acid penetrating through the stone, a little sand being put between the stone and lead. The latter in actual work feels only moderately hot. Between the bottom and the cover of the "saturex" there are several thin partitions, *d d*, which force the fire-gases, entering at 300° or 450° C., to circulate over the level of the acid in *c*; when passing from one of these flues to another they are forced almost through the acid itself, and are therefore quickly brought down to 150° C.; the acid just as quickly gives up its water and even some acid-vapour, and continuously runs off at *j* in the concentrated state into a cooler *o*.

The "recuperator" contains three lower stone plates, *e e e*, and two upper lead plates, *e' e'*, all of them arranged as shown in Fig. 450. Each plate has one hundred holes with somewhat raised margins, so that a thin layer of acid remains standing upon it. The cups, *g g*, made of porcelain with jagged edges, produce a hydraulic seal or at least a great resistance to the passage of the air. The acid arrives as chamber-acid of sp. gr. 1.58 through pipe *x*, and by the overflows *ff* it runs from one plate to another, finally into the satorex. The gases coming from the latter are by an injector drawn through the holes, from underneath the porcelain cups *g g*, and are thus brought into intimate contact with the liquid. *r r'* are thermometers, which serve for regulating the work: the lower, *r*, ought to show about 150° C.; the upper, *r'*, about 85° C. *s* is a pressure-gauge for the aspiration; *k* the pipe leading to the coke-boxes. The concentration can be driven to 98 per cent.  $\text{H}_2\text{SO}_4$ , and the most impure Glover acid can be used, because in the recuperator there is no evaporation, and therefore no formation of crusts;

air and hot acid, but it must be constructed in such a manner that the inevitably formed deposits and crusts do not give any trouble. Under these circumstances the acid can be concentrated far below its boiling-point. In order to produce acid of 95 per cent., boiling at  $284^{\circ}\text{C}$ ., the temperature need not exceed  $170^{\circ}$  or  $180^{\circ}$ ; for the most highly concentrated acid, boiling at  $320^{\circ}$ ,  $200^{\circ}$  to  $230^{\circ}$  is sufficient.

In order to denote both functions of this part of the apparatus visible at *c*, Kessler calls it a "saturex," because it saturates the fire-gases with acid-vapours, and it quenches the greatest part of their heat. The gases enter the "saturex" at  $300^{\circ}$  to  $450^{\circ}\text{C}$ ., and leave it at  $150^{\circ}$ . The acid-vapour contained therein is kept back in the "recuperator" mounted above the "saturex." This part of the apparatus exactly resembles the dephlegmating columns employed in the rectification of spirit of wine. It is fed with chamber-acid, previously employed for cooling the hot, strong acid issuing from the "saturex." This acid is divided over the numerous holes of the top plate, and gradually descends on to the four lower plates of the recuperator. In doing so it meets the hot air and vapour issuing from the saturex, and drawn through the liquid acid by applying suction at the end. In the recuperator the temperature sinks to  $85^{\circ}\text{C}$ .: this causes nearly the whole of the acid-vapour to condense, while the steam is not condensed, nor is there much fresh steam formed here. This is important, since any concentration of the acid in this place would cause deposits which would soon obstruct the holes in the plates.

Although the gases escaping from the recuperator contain next to no real *acid-vapour*, they contain some acid in the shape of *mist*, as well as some vapour of sulphuric anhydride. This mist is retained by two boxes filled with dry coke in pieces about the size of a pea (cf. *infra*, p. 1195); a little water condensing here converts the  $\text{SO}_3$  into  $\text{SO}_4\text{H}_2$ . The weak acid thus formed may be passed through the recuperator. The gases now issue into the air, moderately warm and perfectly free from acid, but charged with all the steam driven out of the chamber-acid. The distilling acid is thus completely condensed without the necessity of employing any cooling-water.

Figs. 448 and 449 show the apparatus. Fig. 448 is a

the hot fire-gases radiate below upon the slabs *d*; through *f* they rise into flue *g*, covered by cast-iron plates *k*, upon which the lead pans *j j* effect the ordinary preliminary concentration.

The acid to be concentrated is kept in a flat trough, *c*, made of Volvic lava, or other material refractory to hot acids, with joints made tight by means of asbestos cement. This vat is surrounded by another vat, *r*, made of lead and resting on iron rails *s*. The surface of the acid in *c* is kept at a distance of from 2 to 6 cm. from the slabs *d d* by means of a valve in the entrance-pipe. The acid comes from the pans *j j* through siphon *g*, and enters through pipes *y y* into an acid-proof chamber, *m*, filled with silex fragments and jacketed with lead. The vapours not condensed here pass into a second chamber, *l*, made of lead and filled with dry coke (beginning with large pieces, gradually diminishing to the size of a grain of wheat), where the vapours are scrubbed and all the sulphuric acid is retained. This weak acid passes back through *p* into the pans *j j*, or elsewhere. From *l* rises a lead pipe, *u*, in which artificial draught is produced by injector *v* to such an extent as to balance the suction of chimney *i*. 2 is a lead cooler with hydraulic joint (similar to that employed in Kessler's hot-air apparatus); 1 a running-off pipe for the concentrated acid, made of Volvic lava covered with cooled lead, burnt on one side to the lead acid-basin and on other side to the cooler 2. 3 is a lead pot for collecting the acid.

The process is worked as follows:—The acid is concentrated in pans *j j* to 60° or 62° Bc., and passes into the Glover-like scrubber *m*, where it meets the vapours formed underneath the slabs *d d*. It arrives hot in the trough *c*, where it is concentrated by radiant heat as it flows on, so that it issues at full strength through *i* into cooler 2. The vapours are partly condensed in the silex scrubber *m*, by contact with the acid running through it, and then pass through the dry-coke scrubber *l*, from which the condensed acid runs away through *p*. The draught in *u* is regulated in such a manner that the air cannot take the opposite way, down *u* and through the interstices in the slabs into chimney *i*. It is also possible to allow some of the fire-gases to pass underneath the slabs *d d*, by means of interstices left on purpose, preferably near the entrance of the acid. Even all the gases may be conducted this way, but then

the chambers *m* and *l* must be made much larger. In this case the heating must be done with coke; but if the slabs *d d* are closely jointed, or if the draughts are properly regulated, wood, coal, oils, or tar may be employed as fuel.

According to the *40th Alkali Inspectors' Report* for 1903, p. 24, complaints were made about the noxious gases discharged from the Kessler apparatus. The *41st Report* states that a great improvement had been effected in this direction, and a still more favourable account is given in the *42nd Report* for 1905, p. 20. The *47th Report* (for 1910), p. 17, states the Kessler plant continues widely in use, and that the large volume of steam accompanying the gases and vapours is removed by driving them by means of a fan through the scrubber, in which the acid bodies are retained as far as practicable (see below).

In the *Monit. Scient.*, 1904, p. 557, Kessler defends his system against faults found with it by Hartmann and Benker. According to his Fr. Ps. 288752 and 305781, for the purpose of preventing the concentrated acid from acting upon the lead, it is made to flow through a heat-exchanging apparatus, in which the fresh acid cools the hot concentrated acid.

Kessler's *condenser for the acid fog* carried away by the gases consists of a lead-lined tank, with a grid of lead-lined iron bars, on which are placed layers of coke powder of gradually diminishing size; the gases are passed in at the top and drawn off at the bottom. A detailed description and drawing is found in *Chem. Trade J.*, 1907, xl, p. 80.

Ph. Meyer's gas filter (*Z. angew. Chem.*, 1906, pp. 1318 *et seq.*; *vide* Chapter XL.) may also be used for this purpose.

The *propulsion of the gases* in the Kessler apparatus is now mostly performed by the hard-lead fans of Paul Kestner (Berlin W35, also branches in London and New York), in lieu of the formerly employed steam-jets. Whereas these consume 900 to 1000 kg. coal per day, the Kestner fans take only 150 kg., working at 3 h.p. The fan is best placed at the end of the apparatus behind the coke boxes, or between these and the "saturex" (*suprà*, p. 1193). The firm Kessler formerly employed cast-iron Pratt fans, but abandoned these, which required 10 to 12 h.p., in favour of Kestner fans, which consume only one-third as much power.

The newest modification of the Kessler apparatus is that

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patented by Teisset and Prat (B. P. 14300 of 1908; Ger. P. 229676; Fr. P. 398212; Amer. P. 993125, and shown in Figs. 457 and 458). The fire-gases, generated in a coke gas-producer, pass through the "saturator" S along its length. This is a pan, made of Volvic lava, placed in a lead shell, *a*; partitions or baffles, *b b*, are arranged in this transversely (not longitudinally as in the former Kessler pans), resting on bearers, *c*, and dipping

FIG. 457.

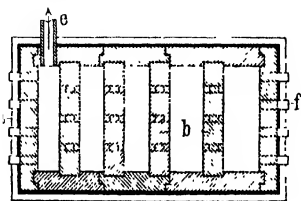
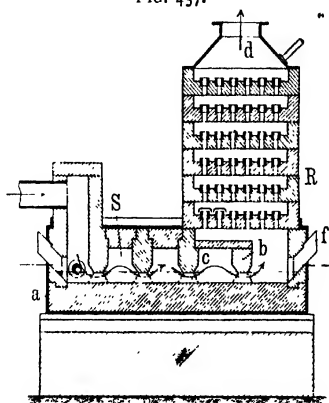


FIG. 458.

a little into the acid. A fan and ejector, placed externally (a special construction of which is described in B. P. 13720 of 1909), draws the gases out, and in being forced underneath the baffles they thoroughly agitate the acid and are brought into intimate contact with it. The baffles can be easily taken out and renewed when worn out. The gases, when leaving the saturator, where they are saturated with aqueous vapour, pass upwards through the "recuperator" R, built of acid-proof material, similar to the spirit-of-wine rectifying columns, with six horizontal plates, *d*,

provided with numerous holes covered by bells. The acid to be concentrated runs in at the top, and is brought into such intimate contact with the gases, rising up through the bell-holes, that the temperature comes down to  $90^{\circ}$  at the top. At this temperature only aqueous vapour but no acid vapour can exist, so that all the acid vapour is condensed before the gases get out; a small quantity of acid, carried away in the shape of fog, is retained by a coke-filter, so that the finally escaping gases are free from acid. The stoppered holes *f* allow of cleaning the saturator. The concentrated acid, which is as clear as water and tests up to 98 per cent.  $\text{H}_2\text{SO}_4$ , is run out of the saturator at *e* into a cooler. The cost of an apparatus for producing 5 tons acid (97 to 98 per cent.) per day is about £1200; the consumption of coke 18 to 19 per cent. In 1911 about 300 such apparatus were at work.

In contradiction to the statement of Hartmann and Benker (*Monit. Scient.*, 1907, No. 782), according to which Kessler's apparatus yields acid not exceeding 95 per cent.  $\text{H}_2\text{SO}_4$ , Gazel (*ibid.*, 1907, p. 368) asserts that the Kessler apparatus, supplied to the British Government in 1898, fulfils the condition laid down, according to which the acid must come up to 1.842. From an English factory he reports the following figures:—

Strength of feeding acid . . . . .	48° Bé.
Strength of concentrated acid . . . . .	65° 9 "
Production per day . . . . .	9100 kg.
Coke used for the gas-producer . . . . .	650 "
Coal used for steam-raising . . . . .	750 "

Lüttgen (*Chem. Zeit.*, 1910, p. 24) considers that the better effect of the new Kessler apparatus is due to acid waves being formed by the hot gases passing through, and impinging against the walls, so that both the effects of splashing and of spraying are produced. Stolzenwald (*Z. angew. Chem.*, 1910, p. 1976) doubts the formation of a spray in this case, and some other advantages claimed for the new Kessler system. According to him, the cost of such an apparatus for producing 5 tons acid 97 to 98 per cent. in twenty-four hours is £1125 to £1200, the consumption of coke 18 to 19 cwt., the power for the face-blast 9 to 10 h.p., the life of the system six years.

If the Kessler apparatus is used for concentrating acid only up to 93 to 95 per cent.  $\text{H}_2\text{SO}_4$ , it can be made smaller and therefore cheaper, and it lasts much longer.

According to Lüttgen (*v. supra*) the Kessler apparatus in its new shape requires 80 to 100 kg. coke for producing 1 ton acid of 92 to 93 per cent.  $\text{H}_2\text{SO}_4$ . The proportion of waste acid is very slight, and so are the costs for repairs. Acid of 98 to 99 per cent.  $\text{H}_2\text{SO}_4$  is obtained with 180 to 190 kg. coke, and there is 200 kg. waste acid of 38° Bé.

Vialleix and Perrin (B. P. 8142 of 1911; Fr. P. 420563) modify the Kessler apparatus by constructing the "saturex" of a single central channel and two side channels through which the hot gases are aspirated. The "regenerator" is made to contain a number of superposed hollow trays, arranged so that the acid overflows from one to another in a zigzag path; contact between the heated gases and the acid is secured by means of transverse ribs which reach from the under-surface of each tray to the level of the acid below, these ribs serving also to strengthen the trays. Lava or stoneware is used in the construction of the channels and trays, instead of the pumice and porcelain hitherto employed.

According to Pohl (*Z. angew. Chem.*, 1912, p. 1851) "vitrosil" (fused quartz, *cf.* p. 1123, 1129, 1147) is greatly preferable to Volvic lava and to porcelain in the construction of Kessler apparatus.

Zanner (B. P. 2379 of 1902) employs cast-iron pans, lined with acid-proof slabs, the joints being cemented with asbestos cement, the corners, etc., being strengthened by protecting pieces so that the primary joints are nowhere exposed to the acid. These pans are placed in the flues leading the gases away from the pyrites-kilns and are fed with Glover-tower acid, which is thus brought up to 93 per cent.  $\text{H}_2\text{SO}_4$  without any extraneous fuel, according to the assertion of the inventor. To protect the acid from flue-dust, the pans are covered with perforated iron (?) or fire-clay slabs. The acid is compelled to flow in a zigzag direction by means of suitable partitions.

According to information received by me from the inventor in February 1902, a set of two pans, 1900 x 400 mm., is capable of supplying per diem 4 tons of acid of 66° Bé. from a mixture of  $\frac{4}{5}$  Glover-tower acid,  $\frac{1}{5}$  chamber acid. The pans had been working continuously for five months, except two cleaning shifts purposely interposed. The weak-acid pan lasted five months, the strong-acid pan seven months, and both might have lasted longer if mistakes had not been made in the lining

provided with numerous holes covered by bells. The acid to be concentrated runs in at the top, and is brought into such intimate contact with the gases, rising up through the bell-holes, that the temperature comes down to  $90^{\circ}$  at the top. At this temperature only aqueous vapour but no acid vapour can exist, so that all the acid vapour is condensed before the gases get out; a small quantity of acid, carried away in the shape of fog, is retained by a coke-filter, so that the finally escaping gases are free from acid. The stoppered holes *f* allow of cleaning the saturator. The concentrated acid, which is as clear as water and tests up to  $98^{\circ}$  per cent.  $\text{H}_2\text{SO}_4$ , is run out of the saturator at *e* into a cooler. The cost of an apparatus for producing 5 tons acid (97 to 98 per cent.) per day is about £1200; the consumption of coke 18 to 19 per cent. In 1911 about 300 such apparatus were at work.

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bearers *c* and *b*, rest the cast-iron pans *a*, lined with stoneware plates *e*, cemented with asbestos and silicate of soda. The size of the plates is chosen in such a manner that the joints are

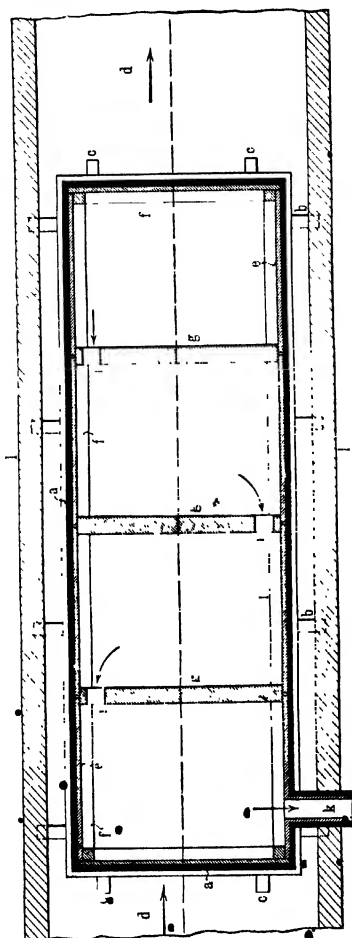


FIG. 461.

covered by the upright stone plates *g*, which hold down the bottom plates in their places, and which also cause the acid to run in a zigzag stream, by the openings *i i* (cf. the sectional plan Fig. 461). The corners are secured by stones *f f*, so that

no primary joints are exposed to the acid. The pans are covered by plates *o*, with holes *n*, protected against flue-dust by caps *m*. Where acid of 97 or 98 per cent. is to be made, several pans are combined, the first of which has no stoneware lining on its bottom. The acid is fed in by the porcelain-lined iron tube *h*, and it leaves by the cast-on lip *k*, lined with stoneware passing through the brickwork *l*. The steam and acid-vapours pass along with the pyrites-kiln gases into the Glover tower; also any nitrous vapours, when waste nitrating acids (from nitrobenzene, nitroglycerine, etc.) are to be concentrated. It is best to provide a by-pass for the kiln-gas, for the purpose of cleaning or repairing the pans. The yield of acid of  $55\frac{1}{2}^{\circ}$  B $\acute{e}$ . per square metre (10.76 sq. ft.) of pan-bottom per twenty-four hours is from 30 to 48 cwt., according to the heat of the gases and the feeding-acid, and its previous concentration. Much more work could be performed when working the apparatus with a vacuum; and it can be also worked by any other source of heat. There is absolutely no expense for fuel, and next to none for supervision; the cost of plant is very slight. In *Z. angew. Chem.*, 1907, p. 8, Zanner defends his plan against objections made to it by Hartmann and Benker (*ibid.*, 1906, p. 566).

W. R. Quinan (Amer. P. 699011; *J. Soc. Chem. Ind.*, 1902, p. 772) constructs behind the pyrites-kilns a "mixing-chamber," provided with an iron roof, covered with infusorial earth or the like, which near its top leads to an ascending inclined flue, the bottom of which is formed of steps made of Volvic lava. These steps possess upwardly extending flanges at the back and sides, and a downwardly extending lip or flange at the front end, overlapping the back flange of the next lower step. This inclined flue may be connected directly with the first chamber, or, preferably, with the Glover tower, from which the acid runs down the Volvic steps, and arrives in a highly concentrated state in the mixing-chamber.

Gaillard (B. Ps. 23841 of 1905, 12538 of 1906; Amer. Ps. 856048, 859757, and 859759; Ger. P. 192155; Fr. P. 367376) concentrates sulphuric acid by running it down in fine jets or sprays in a tower (*a*) in which hot air from a coke fire ascends. A second tower, or a coke chamber, serves for condensing the acid carried away by the hot gases. The towers are made of

an acid- and fire-resisting material, and have an outside lead casing, a hydraulically sealed top, and a sieve plate near the bottom; the acid collecting there is cooled by a cold-water coil. Some details on this process are given in *Chem. Trade J.*, xlii. p. 60, and by Lüttgen (*Chem. Zeit.*, 1910, p. 24). A very complete description of it, with many diagrams, is made by Recke (*Chem. Zeit.*, 1910, pp. 173 and 182), and of this we here give an abstract:—At the outset it is stated that up to that time (the end of 1909) upwards of 100 such apparatus had been built and set to work. The gas-producer, *c*, Fig. 462,

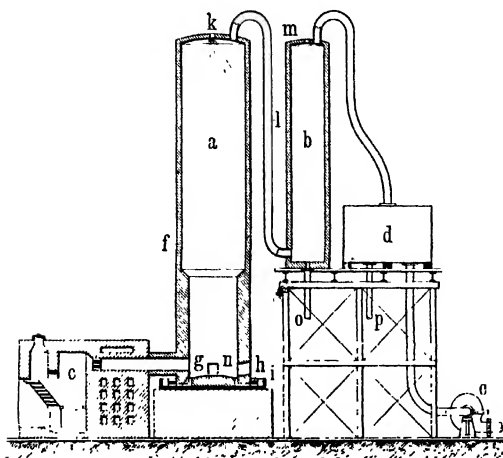



FIG. 462.

belonging to it is worked with coke; it is 3 m. high, 4 m. long, 2.8 m. wide, and costs £45. The concentrating-tower *a* is 15.5 m. high, and consists of 15 Volvic rings, superposed over one another without any mortar or cement. It is empty, without any "packing." Each ring consists of 8 lava blocks, held together by lead-covered iron rings. The blocks have V-shaped, longitudinal grooves, so that at the junction of each two blocks a canal of  shape is formed which is filled with a putty of water-glass and Volvic powder. The tower at the bottom has an inner width of 1.70, at top 2.0 m.; the thickness of the walls is 450 mm. at the bottom rings, 400 mm. at the fourth rings, 250

mm. at the three following rings, 200 mm. at the three following, and 150 mm. at the four top rings. The top of the tower is formed of four Volvic plates, with an inlet for the spray-nozzles, and a 500 mm. outlet for the waste gases. The bottom of the tower is formed by a tray, 400 mm. high, with twelve outlets for the hot, strong acid. This acid is cooled by a tubular cooler, 80 m. long, placed in the bottom tray round the tower.

The cost of a concentrating-tower is £1040. It is connected with a recuperating-tower, *b*, 8 or 10 m. high, 1.51 m. wide outside, 1.34 m. inside. It is placed on a wooden or iron frame at such a height that its top is at the same level as that of the concentrating-tower. The recuperating-tower is made of 4 mm. lead, lined with 80 mm. stoneware plates, and held together by a frame of wood and iron. It has two spray-nozzles at the top and an outlet for acid at the bottom, and is connected by *d* with the top of the concentrating-tower by a Volvic or stoneware pipe, 500 mm. wide, descending from the latter and entering into it near the bottom. It costs £80. Then follows a coke-filter *e*, a wooden box lined with 3 mm. lead, 3 m. high, 7 m. long, and 5 m. wide, into which the gases enter from the top, going out at the bottom. The coke rests on a grate of acid-proof bricks, and is graduated in size from 60 to 100 mm. at the bottom to 5 to 15 mm. at the top; the filter costs £170. Last of all comes the fan, *e*, consisting of a lead case and iron wings, protected against the acid by an ebonite casing; entrance-pipe, 400 mm.; exit-pipe, 400 × 290 mm.; 650 revolutions per minute; power required, 1 h.p.; cost, £49. There are also two acid-eggs, costing £115. The whole plant costs £1532.

The work is carried on as follows. The gas-producer *c* is charged every two or three hours with coke of 40 mm. size; this should be dry and free from non-coked coal, which would impart a brown colour to the acid. The gas meets air preheated by a fire-brick grating, and the flame formed enters at *g* into the bottom of the concentrating-tower *a*, where it meets the chamber-acid, converted into a spray by appropriate nozzle *k*, and air compressed to  $1\frac{1}{2}$  or 5 atmos. The concentrated acid flows through a cooler in the bottom tray. The gases leave the tower at its top and enter the recuperating-tower *b* at a temperature of 100° to 200°, where the acid-fog is partly

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condensed, to acid of 57° Bé. The uncondensed gases pass through the coke-chamber *d* into the fan *e*, and then into the outer air. The loss of acid in the gases is only 0.2 to 0.3 per cent.; the strength of the concentrated acid can easily be brought up to 98 per cent.  $\text{H}_2\text{SO}_4$ ; it is almost devoid of colour, and contains only about one-third of the iron and one-fourth of the arsenic brought in by the chamber-acid. The salts secreted during the process accumulate at the bottom of the tower, and can be taken out by a cleaning-hole, *n*. The acid from the recuperating-tower (57° Bé.), either goes back to the concentrating-tower, or is sold as it is; the acid from the coke-box is passed through a Glover tower, or used anyhow.

Gaillard guarantees the following results to be obtained by his system, when starting with chamber-acid of 54° Bé.:—

Production in 24 hours.	Percentage of $\text{H}_2\text{SO}_4$ in the acid produced.	Consumption of coke per cent. of the acid produced.
4 to 6 tons	97 to 98	20 to 25
8 " 10 "	92 " 93	8 " 12
30 tons	60° Bé.	3 " 6

The following statements refer to the cost of the process per ton of acid produced.

	Acid of 97/98 per cent.	Acid of 95/96 per cent.	Acid of 93/94 per cent.	Acid of 80° Bé.
Wages . . . . .	4½d.	4d.	2½d.	1d.
Motive power for gas and acid . . . .	½d.	½d.	½d.	1½d. to ½d.

Repairs are principally required for the lead cooling-pipe; the process is not yet long enough at work to say anything on the other parts of the plant.

In 1911 about 100 such apparatus were stated to be at work.

Stolzenwald (*Z. angew. Chem.*, 1910, p. 1976) objects to the plan that the acid must be most carefully filtered, in order not to stop up the spray-producer and thereby also to damage the shell of the tower. The life of the plant is about six years. The cost of it is much higher than that of the Kessler plant, and more coke is used for heating than in the latter. Most certainly

it cannot be used for regenerating waste acid from the refining of petroleum, etc. The only plan suitable for this, as Stolzenwald claims, in order to get from such waste acids an acid of 97 to 98 per cent.  $\text{H}_2\text{SO}_4$ , is described in his own Ger. Ps. 212000 and 213589 (*suprà*, p. 1182).

Duron (*Z. angew. Chem.*, 1910, p. 2307) contradicts Stolzenwald in several points. According to him, acid of 67 to 98 per cent. can be made in direct manner, and economically, both by the Kessler and the Gaillard apparatus. With the Kessler apparatus the cost is slightly less than by the old system. The Gaillard apparatus, which is in reality a Glover tower, made of Volvic lava without packing, lasts much longer than six years; such lava is not attacked by the impurities of sulphuric acid, and this acid does not require filtering, in order to pass the openings of 4 to 6 mm. width. Such an apparatus for producing 8 to 9 tons acid 97 to 98 per cent. costs £2250 to £2500, and requires 15 to 17 per cent. coke and  $\frac{1}{2}$  to  $\frac{3}{4}$  h.p. for the fan, as proved by many testimonials in Duron's possession (he is chief engineer of the firm E. Hartmann, formerly Hartmann & Benker). The Kessler apparatus also permits concentration to 97 per cent., but consumes much more fuel (30 per cent.), and yields only 4 tons per diem. The improved Kessler apparatus (system Teisser-Prat, p. 1198) does not show as much advantage as expected. The employment of Volvic lava requires other arrangements than the use of pumice, as its mechanical resisting-power is less. Such a new apparatus costs £2250 to £2350 for a daily make of 4 tons 97 to 98 per cent. acid, with 22 per cent. coke and 10 to 12 h.p. for the fan. Another improvement of the Kessler apparatus, by Duron himself, has turned out successful in quite a number of cases; for making 5 to 6 tons acid 97 to 98 per cent. it costs £1050; requires 16 to 18 per cent. coke and 4 h.p.

In the case of acids forming crusts of ferric sulphate during concentration, Löwy and Klagsbrunn (Austr. P. appl. A6792 of 1909) modify the work of the Gaillard towers by collecting the hot acid, as it arrives at the bottom, in an acid-proof dish provided in that place, and running it from there into an outside settler, from which the clarified acid flows into another concentrating-apparatus, surrounded by hot producer-gases, and then enters the tower.

Duron (Fr. P. 430145) enriches sulphuric acid by  $\text{SO}_3$ , produced by the dissociation of a portion of the concentrated acid by means of heated air, the waste heat of which is then utilised for the concentration of the dilute acid in a "concentrator" and a "regenerator"; the air is finally deprived of the last traces of acid in a condenser. Dilute acid is supplied to the regenerator where it is concentrated by the heated gas, and part of this acid is then used in the lowest stage of a "separator" tower for absorbing water from dissociated acid vapours, the upper part of the tower being fed with 96 to 98 per cent. acid from the concentrator for the absorption of the  $\text{SO}_3$  from the same vapours. The concentrator receives most of the acid from the regenerator (situated above it), and is so arranged that the heated air passes rapidly in a thin layer over the surface of the acid without giving rise to agitation of the liquids.

The Swedish Nitro Syndicate, Stockholm (B. P. 10591 of 1908), claims the continuous production of concentrated acids in a vertical column of acid-proof material filled with pieces of similar material, heated both on the outside and inside by a current of hot gases.

Proelss (Amer. P. 989537) describes an apparatus for making concentrated sulphuric acid, comprising a denitrating-chamber, a concentrating-chamber, and cooling-apparatus, conduits for passing burner-gas into the chambers and for discharging the gases from the chambers into cooling-apparatus. Lead chambers receive the gases from the cooler. This apparatus is an improvement upon former patents, Amer. Ps. 963174 and 963175 and 967174.

Lüttgen (*Chem. Zeit.*, 1910, p. 23) points out that the Volvic towers, in which a spray of chamber-acid is produced for concentration by hot gases, require very pure acid, to prevent frequent stoppages of the spray producer. Consumption of coke for 1 ton acid 92 to 93 per cent. = 110 to 120 kil. The cost of repairs must be rather high.

For the concentration of sulphuric acid by hot gases, R. C. Forster (*Chem. Zeit.*, 1910, p. 734) recommends the new high-pressure fans, made of hard lead by Kestner, as more efficient and economical than the Kessler or other fans hitherto used.

Kaesmacher (B. P. 2382 of 1908; Fr. P. 386783) separates nitric acid during the concentration of sulphuric acid by finely

dividing the acid liquid by refractory materials in a suitable tower and subjecting it to the action of hot air.

*Concentration of Sulphuric Acid in Vacuum-Retorts.*

A very interesting concentrating method, including the use of Field tubes, formed part of an ingenious, but over-complicated system of the manufacture of sulphuric acid invented by De Hemptinne, of Brussels, and described at length, with diagrams, in our first edition, pp. 507 to 512, to which description we simply refer, as De Hemptinne's process has never been carried out in full and is decidedly impracticable. Another ingenious process of his, described and illustrated in our first edition, pp. 513 to 516, seeks to carry out an idea previously proposed by several other inventors, *e.g.* Kuhlmann (in 1844), viz., concentrating sulphuric acid in a *partial vacuum*, and thus reducing the temperature to such a point that the whole operation can be carried on in lead. As this process, which was actually at work for some time, has not proved successful, we also refer for it to our first edition. A further modification of his plan has been described by De Hemptinne in the *Bull. Musée Industrie Belg.*, January 1882.

Of more modern forms of leaden vacuum-apparatus we shall mention that of Krell (Ger. P. 118880). The acid flows through a lead pipe, *a*, Fig. 463 (p. 1210), heated by an oil-bath, *b*. Pipe *a* is stiffened inside against atmospheric pressure by diaphragms *c c*, leaving passages for the acid in such a manner that the acid must proceed in a zigzag course, and provided with communications in their upper part for the vapours. At the bottom of pipe *a* lies a perforated pipe, *t*, through which hot gases may be introduced for the purpose of hastening the concentration. The unperforated diaphragms *f f*<sub>1</sub> stiffen the pipe and divide the steam-space into three compartments, connected through *h h*<sub>1</sub> *h*<sub>2</sub> with a common vacuum-pipe, *i*. In this way the coolers *k k*<sub>1</sub> *k*<sub>2</sub> will condense acids of various strengths. The acid entering as chamber-acid of 50° Bé. leaves as acid of 64° or 65° Bé. [that is, we must notice, only 86 to 90 per cent. H<sub>2</sub>SO<sub>4</sub>!] and descends through a pipe, *m*, which must be at least 17 feet long, into a collector, *n*. By surrounding *m* with a jacket, *o*, the heat of the outflowing acid can be utilised for heating up the chamber-acid. Oil-bath *b* is heated indirectly by means of coil



## 1210 THE CONCENTRATION OF SULPHURIC ACID

$q$ , heated by a fire,  $p$ , and connected at both ends,  $r$ ,  $s$ , with the oil-bath in such a manner that a constant circulation takes place. [According to private information, Krell employs lead alloyed with a little copper, as recommended by me for higher temperatures and strengths, cf. p. 326.]

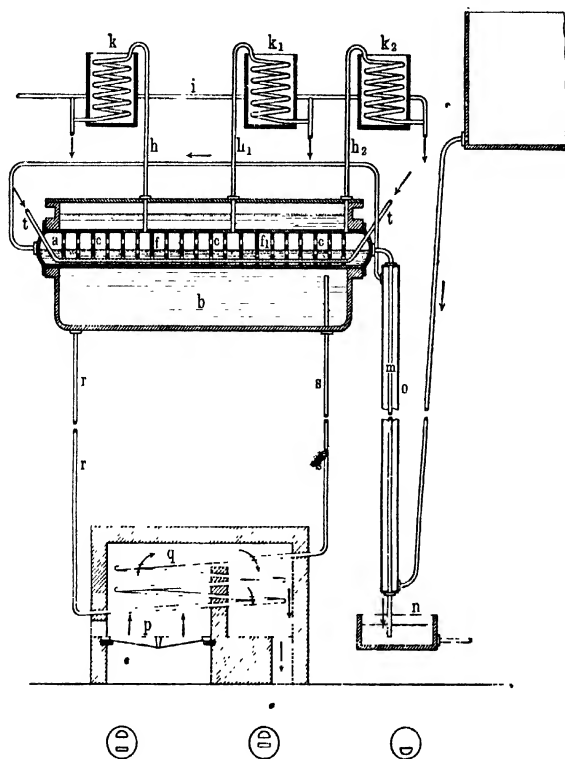


FIG. 463.

Cast-iron retorts are also used to concentrate sulphuric acid in a vacuum, starting from such strengths at which the cast-iron is not yet acted upon.

Fig. 464 shows the shape of cast-iron vacuum-retorts used in Germany for sulphuric acid with great success and furnishing very high-strength acid. Such a retort weighs about  $7\frac{1}{2}$  tons.

J. Meyer (Ger. P. 71580) combines a lead vessel with an



Brown and Georgeot (Fr. P. 241815) state a theory as to the concentration *in vacuo* in which there is nothing new.

The Kommanditgesellschaft L. Kaufmann & Co. (Ger. P. 134773) concentrate sulphuric acid in a cast-iron vacuum-still by means of a steam-jacket or gaseous fuel, driving it over the heating-surface in layers of only 10 to 15 mm. depth by means of stirrers almost touching the metal, with such a velocity that the concentrated acid by its centrifugal force can issue continuously in spite of the vacuum. By the above treatment the steam-bubbles are more easily detached from the solid surfaces.

Cast-iron vacuum-retorts are most suitable for treating the *dirty acid* (acid-tar, sludge-acid) formed in the chemical treatment of mineral oils (*cf.* pp. 1179 *et seq.*). This acid, when boiled for some time, chars most of the organic substances dissolved by it, and is at the same time concentrated. But in this process much of it, sometimes nearly 20 per cent., is reduced to  $\text{SO}_2$  (*cf.* p. 1181), which causes not merely loss, but also great nuisance, unless the  $\text{SO}_2$  can be reconverted into  $\text{SO}_3$  (*cf.* Chapter XI.) or otherwise utilised. This difficulty is overcome by the employment of vacuum-retorts. The considerable lowering of the boiling-point thus produced causes the action of the acid on the organic substance to be much less and of a different kind. There is only about 3 per cent. lost as  $\text{SO}_2$ , and the organic substance is converted mostly into a carbonaceous substance which can be removed by filtration through sand. The acid thus made is  $=66^\circ \text{Bé.}$ ; it is dark-coloured, but quite fit to be used over again for the refining of mineral oils.

Kynoch & Co. and Cocking (B. P. 28891 of 1896) employ cast-iron retorts working with a vacuum for the concentration of waste acid from nitroglycerine.

The Gräflich von Landsberg Chemische Fabrik (Fr. P. 432873) first concentrate the acid at  $150^\circ$  to  $160^\circ$  to about  $61^\circ \text{Bé.}$ , and then introduce it in a finely divided state into a tower or other appropriate apparatus in which a partial vacuum is maintained, and in which the temperature is regulated by the admission of heated air.

*Concentration of Sulphuric Acid by Electricity.*

Bucherer (*Chem. Zeit.*, 1893, p. 1597) makes the following calculation:—The production of 100 kg. acid of 66° Bé. from 117 kg. acid of 60° Bé. requires 32,679 large calories, corresponding to

$$\frac{32679 \times 4.2 \times 10^3}{736 \times 3600} = 44.2 \text{ electrical h.p. hours;}$$

calculating the electrical h.p. hour =  $\frac{1}{2}d.$ , the above is equal to £1 per ton (on the large scale). Further estimates of the amperage and voltage, the platinum surface, etc., must be passed over here as being entirely hypothetical.

Häussermann and Niethammer (*Chem. Zeit.*, 1893, p. 1907) have made actual experiments on this point. As might be expected, only alternating currents can be employed, since otherwise an electrolysis takes place. The concentration is very easy, but requires 1490 watt-hours per kg. This seems to exclude every possibility of practical application.

Peuchen and Clarke (B. P. 24739 of 1893) propose both purifying and concentrating sulphuric (and acetic) acid by the electric current, eventually proceeding up to distillation. They propose electrodes mechanically revolving round a hollow shaft within the boiling acid! A fresh patent of theirs (Ger. P. 83526) describes stationary electrodes for the same purpose.

Wacker (B. P. 3183 of 1895) proposes concentrating sulphuric acid by electricity, with introduction of  $\text{SO}_2$ .

Johnson (Amer. P. 825957) concentrates sulphuric acid containing  $\text{SO}_2$  by an electrolytical treatment which oxidises the  $\text{SO}_2$ ; more of this is constantly introduced.

*Protection against Leakage of Acid into the Cooling-water.*

Will (Ger. sample protection, No. 416830) places in the cooling-water two zinc plates which are filled with clamps above the water-levels, and which in case of any acid leaking into water electrolytically set an alarm into motion.

;

*General Remarks.*

Loew (*Z. angew. Chem.*, 1896, p. 259) gives some calculations with respect to the work done by concentrating-apparatus for

sulphuric acid. In the case of platinum stills the work performed is in inverse proportion to the strength of the acid distilling off; the stronger the distillate, the less concentrated acid is produced, although even more fuel is consumed in the former case. Any contrivances, like Prentice's corrugated bottoms or partitions, inside a long still which diminish the mixture of the dilute acid entering and the concentrated acid leaving the still are useful in this direction. Turning to the concentration by hot air or fire-gases, we can calculate the amount of fuel required, if we ascertain the necessary data. Thus, for instance, if the gas leaves the apparatus at a temperature of  $80^{\circ}$ , and saturated with steam, we shall require 6.12 parts of carbon to produce 100 parts acid of 95.6 per cent. from the corresponding quantity of acid of 64.5 per cent., assuming the latter to enter at  $20^{\circ}$  C. and the former to issue at its boiling-point. Fuel producing steam during its combustion is less advantageous than coke.

*Monohydrated Sulphuric Acid.*

For some purposes sulphuric acid containing no water, or hardly any, and corresponding as nearly as possible to the formula  $\text{H}_2\text{SO}_4$ , is required. Such acid is extremely useful in certain nitrating and sulphonating operations, connected both with the manufacture of explosives and that of colouring-matters. So great, indeed, has been the want of such a monohydrated acid, that many manufacturers made it by mixing ordinary rectified oil of vitriol and Nordhausen fuming acid, in which case the  $\text{SO}_3$  contained in the Nordhausen acid combines with the excess of water existing in the rectified O.V. to form  $\text{H}_2\text{SO}_4$ . This was, however, formerly a costly process, as is shown in our second edition, pp. 738 and 739, and therefore I worked out another process. At the present day the cheapening of fuming O.V. produced by the contact method makes this process unnecessary, but as it is carried out on a new principle we shall retain its description here.

My proposal, *freezing out* the monohydrate from good rectified O.V. (Lunge's B. Ps. 96 of 1883 and 4430 of 1887, the former communicated to Walter Weldon, the latter to John Brock), has been carried out with full success at several alkali-works.

Sulphuric acid is concentrated in platinum or iron stills to

97 per cent.  $\text{H}_2\text{SO}_4$ , or a little more, if convenient, and is then cooled down in the usual manner. It is then conveyed by air-pressure or in any other suitable manner to the store-tank A, placed at a somewhat higher level than the "charging-box" B of the freezing-machine (Figs. 465 to 468). Instead of running the acid directly from A into B, it is conveyed down to the ground-level in a conduit C, in which is interposed a cooling-worm or other refrigerating contrivance, D. The pipe C, with an interposed shutting-off tap, E, rises a little above the top of the charging-box B, and then descends into the top of this box. The object of tap E is to shut off the communication between A and B during the time a charge is being blown out of B.

The charging-box B is made of iron, and is of such a shape that it stretches from side to side right across the tank containing the freezing-cells. It is divided by vertical partitions into the same number of divisions as that of one row of iron freezing-cells G, and each of these divisions is made of such size that on blowing out its contents it exactly fills one of the cells, G, to a suitable height. The partitions do not reach quite up to the lid of the charging-box B, so that all the divisions are filled by the supply-pipe C from the store-tank A, and their contents are forced out simultaneously by means of the compressed air acting through a pipe K inserted into the lid of the charging-box. Pipe K rises to a higher level than the top of the store-tank A before descending to the air-pump; consequently when A is put into communication with B, the acid fills the entire box B and rises in the air-pipe K up to the level of the store-tank, but it cannot overflow into the air-pump. Pipe K is provided with two taps, of which L communicates with the air-pump, and M with the open air; the latter tap is opened while the box is being charged with acid, and is shut immediately afterwards.

Each of the divisions of box B is provided with a discharge-pipe, H, which begins immediately over the curved bottom of the box, passes out of the lid, and rises upwards so far that no acid can overflow during the charging of B from the store-tank A. The discharge-pipes H H then descend side by side, so that the lower end of each is just above one of the freezing-cells G. Thus, as soon as the compressed air begins to act

upon the surface of the acid contained in the box, all the discharge-pipes begin to play simultaneously, and all the freezing-cells belonging to that particular row are filled at the same time. When this has been done, a leaden dish, J, is brought underneath the ends of the pipes, to catch the acid draining out of them and convey it away. The row of freezing-cells, which is suspended in an iron frame, N, is moved by means of a travelling-crane, O, to the other end of the freezing-tank F, which contains a number, say 10 or 15, of such rows of freezing-cells. The space between the cells is filled with a solution of calcium chloride, kept at a low temperature, say  $-20^{\circ}\text{C}$ ., or somewhat more or less, by means of any convenient cold-producing machine. Each time a fresh row of cells has been filled the frames containing the other rows, which rest on pulleys, are moved towards the front end of the tank, so as to allow of the last row of cells being lowered into the back part of the freezing-tank.

When the row of cells which has been longest in the freezing-tank has been sufficiently cooled down, it is lifted out by means of the travelling-crane O. The cells are then dipped for a few seconds into a vessel containing warm water, in order to detach the frozen mass from the sides of the cell by superficial fusion; and when this has been effected the cells are lifted out and are tilted into a spout or trough, P, care being taken to prevent any of the water adhering to the outside of the cell getting into the spout. The spout P contains an Archimedean screw, Q, which crushes up the frozen mass and conveys it into a cast-iron centrifugal machine, R, placed beside the apparatus. The cells G are then righted again and are ready to receive another charge of rectified oil of vitriol. By the action of the centrifugal machine R the frozen mass is rapidly separated into a white crystallised mass of monohydrated sulphuric acid and a mother-liquor consisting of less concentrated acid. The latter is either sold in this state (it is equal in strength to good rectified O.V.), or is brought up to full strength by the ordinary processes of concentration. The solid monohydrate is scooped out of R into a pan, S, made of iron enamelled inside, and surrounded by a warm-water jacket; here it is melted, and is, by means of a tap, run out into carboys or other vessels intended for storing and carrying the product.

My just-described process for manufacturing monohydrated sulphuric acid by freezing was carried out on a large scale in Germany (Griesheim), France (Petit-Quevilly), and England (Widnes), and worked for many years. Only in 1900 it was given up at Griesheim, having become unremunerative through the cheapening of fuming sulphuric acid, in consequence of the development of the contact processes for the manufacture of sulphuric anhydride.

Osterberger and Capelle describe this process, as carried out at Petit-Quevilly, almost exactly as above (*Bull. Soc. Ind.*, Rouen, 1889, p. 307; *J. Soc. Chem. Ind.*, 1890, pp. 390 and 507).

Moranie (*Ann. chim. analyt.*, Sept. 1909) gives an analysis of acid of 66° Bé., obtained by freezing for twenty-four hours at  $-2^{\circ}$  to  $8^{\circ}$ , showing a remarkable degree of purity.

A proposal by Messel (B. P. 1201 of 1878) to prepare monohydrated sulphuric acid by passing pyrites-kiln gases through concentrated sulphuric acid, in order to absorb the  $\text{SO}_3$  contained in the gases, need only be mentioned here.

#### *Packages for Sulphuric Acid.*

Sulphuric acid was formerly always, and is even now to a great extent, sent out in large glass bottles or *carboys* of about 15 gallons capacity, packed in baskets with straw, the projecting necks being still further protected by straw ropes. They are closed by earthenware stoppers dipped in melted brimstone and put in quickly before the sulphur has solidified. Mostly damp clay is put round the top and a linen rag is tied all over it. Often, especially for short distances, the brimstone is omitted. The baskets last only a short time when exposed to the weather and the damp soil, and especially when any acid gets at them. This is sometimes difficult to avoid: after the first use a few drops of acid run down the neck of the carboy and find their way to the bottom of the basket; and the floor of the warehouse, where they are placed, is not easily kept entirely free from acid. Therefore the bottom of the basket is damaged first; and on lifting the carboy the bottle filled with acid sometimes forces out the bottom of the basket by its weight and falls through. For this reason a damaged basket ought never to be sent out; some works go upon the principle of *always* packing the returned carboys in fresh



baskets. The baskets stand much longer when they are dipped two-thirds of their height in coal-tar. In England, baskets made of stout iron wire or of thin hoop-iron are commonly used, protected against quick rusting by a thick coating of coal-tar. In the north of England frequently, sometimes also in Germany, carboy-tubs are used, made of small staves, tapering a little downwards, and bound with iron hoops; the bottle is put in, packed in straw, with only its neck projecting; a circular cover, provided with a hole for the bottle-neck, is put on and fixed. These tub-carboys are rather clumsy and somewhat dearer than basket-carboys, but much more durable; and they afford the great advantage that railways, barges, etc., carry them in two tiers one above the other, which they never do with basket-carboys.

In America, cubical cases are employed, kept together by iron hoops; the bottles are put in with sea-weed; they cost one-third of a dollar per cwt. In France, and also at Aussig in Bohemia, stoneware jars of the size of ordinary glass carboys, and of the same clay as is used for "bombonnes" (acid-receivers), are frequently employed; these can be moved about at the works without baskets, but must be put into baskets for sending out. At Beauvais, where they are made, they cost  $1\frac{1}{2}$  franc each.

Sometimes the glass carboys are surrounded with infusorial earth, which in case of breakage absorbs the acid, whilst in the case of the ordinary straw-packing it runs out and may injure the men or damage railway-trucks. (This way of packing is especially useful in the case of nitric acid, which may cause a fire when coming into contact with straw.)

A special kind of carboy-hampers has been patented by Garneri (B. P. 3190 of 1883). "This basket is built up of numerous standards of wood, thin and elastic. The base is preferably composed of two conical and concentric rings, thin, and of 5 to 6 cm. (= 2 to  $2\frac{3}{8}$  ins.) in diameter. The standards are bound and fixed at equal distances between the two conical rings. Wooden rings, placed at intervals in the height of the basket, are fixed both on the exterior and interior by means of a jointed mould, which gives to the basket the desired contour, according to the carboy or other article it is intended to contain."

Schleicher (Ger. P. 18112) employs tight-fitting wickerwork baskets, the upper part of which is removable and is connected with the lower part by wire fastenings. This plan is shown in Fig. 469. *b* indicates the glass, *e* the joint between the two parts of the wickerwork, *e*<sub>1</sub> the removable part of the latter, *c* *d* the cover.

The Marple Chemical Co., Marple, near Stockport, sells "Carboy Protectors" for the tops of acid-carboys, as shown in Fig. 470, which admit of stacking up to four tiers of carboys over one another without any risk of breakage.

Mauser (B. Ps. 11095 and 21986 of 1902) provides the hampers with a top kept down by springs, or suspends the carboy in the hamper by springs.

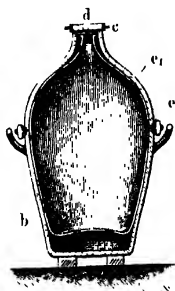


FIG. 469.

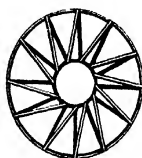


FIG. 470.

Junckers (*Chem. Zeit.*, 1902, p. 582) employs for filling acid-carboys a new kind of funnel, closed at the top. Only two openings are left, one of them for inserting the pipe or tap from the filling-vessel, the other one, provided with a neck, for conducting away any vapours formed. By making the joints with the feeding-pipe or tap and with the neck of the carboy tight by means of india-rubber washers, any loss and damage to the carboys through acid splashing about is avoided.

Mann (Ger. P. 189834) describes a contrivance for closing carboys in such a way that the channel for allowing gases to get out is not in constant communication with the outer air, but automatically opens when a certain tension has been reached, and again closes by itself when this tension is lowered.

Figs. 471 and 472 show this. The ball *o* opens into the chamber *n*; to prevent *o* from falling out, a bandage *p* is fastened over the orifice of *n*; it possesses a small hole for the vapours to escape.

Several contrivances have been invented for *emptying acid-carboys*. Some of them consist of iron frames adapted for tilting, others of apparatus adapted to the carboy-necks and acting on the principle of a chemist's wash-bottle, the necessary air-pressure being produced by a small force-pump or by an india-rubber bag with treadle. These and other contrivances are described by Oppler in his report on the Berlin Exhibition of Apparatus for preventing Accidents (*Chem. Ind.*, 1889, p. 528). Cf. also the siphons, etc., shown, pp. 696 *et seq.*

The Aktiengesellschaft für Anilinfabrikation at Berlin has patented (Ger. P. 8305; Wagner's *Jahresber.*, 1880, p. 236) an

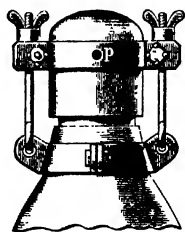


FIG. 471.

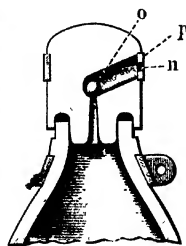


FIG. 472.

apparatus for carrying acid-carboys without in any way putting stress on the handles or other parts of the hampers, so that the carboys can be safely handled even in rotten hampers. Other contrivances of this kind consist of hand-trucks, on which the carboys are suspended from chains, as shown in Fig. 473.

Nevertheless it frequently happens that glass carboys get cracked, either in handling or by the jolting of railway trucks; and the acid running out is not merely lost, but often does a great deal of damage. The railway and steamboat companies accordingly will only accept acids (sulphuric acid, as well as other mineral acids sent in carboys) at the sender's risk, or else at very high rates for carriage, and only send them by certain trains. Under all circumstances, on account of the bulky nature of this merchandise, a very much higher rate is charged for its conveyance than corresponds to its weight. A truck which

carries 10 tons of goods in casks can only carry about  $2\frac{1}{2}$  tons of vitriol in carboys. The additional cost of carriage is therefore in direct proportion to the accompanying dead weight and bulk; and as such the water must be regarded which is contained in acid of  $144^{\circ}$  Tw. (brown vitriol) over and above that in strong vitriol.

The cost of carboys also amounts to a good deal. It differs very much, according to whether the situation is more or less convenient for purchasing the bottles, etc.; but it will hardly ever be under £2 per ton of real acid, and is proportionally much higher for brown vitriol containing 78 per cent. of  $\text{SO}_4\text{H}_2$ .

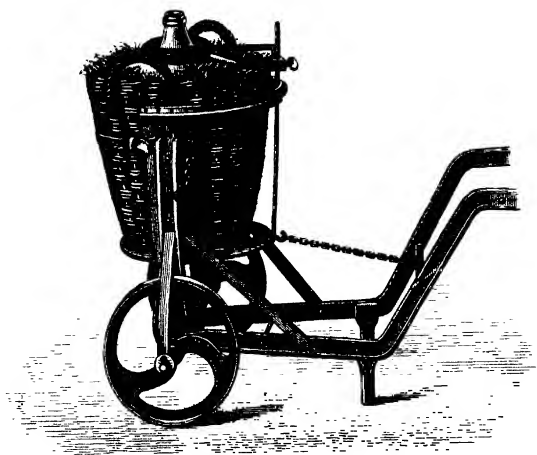


FIG. 473.

than for strong vitriol with 93 per cent. of  $\text{SO}_4\text{H}_2$ . Of course, the empties are mostly returned; but there is always much breakage, and for longer distances the return-carriage is too dear.

It follows from this that it will only pay for a certain distance, differing very much according to local circumstances, to send out brown vitriol of  $144^{\circ}$  to  $152^{\circ}$  Tw. in glass carboys; when the distance exceeds that limit, the extra cost of packages and transit becomes equal to or more than the cost of extra concentration, and the consumers prefer to buy strong vitriol of  $168^{\circ}$  Tw. Habit or, more strictly speaking, ignorance causes some consumers to buy acid of  $168^{\circ}$ , when  $140^{\circ}$  or even chamber-acid would do quite well.

As reported in the *Chem. Trade J.*, 1911, xlviii. p. 568, the English Railway Companies have adopted the following rules for the conveyance of acids in carboys:—

*Definition of Carboys.*—The term "carboy," as used in this classification, means a globular bottle of not less than 12 gallons' capacity, made of glass not less than  $\frac{1}{8}$  in. thick in any part, free from striae and bubbles, carefully annealed, and with the initials of the maker on the neck.

*Packing.*—The carboy must be firmly packed in a hamper of iron or wickerwork, with a minimum thickness of  $\frac{1}{2}$  in. of straw packing between the hamper and the carboys. This packing must be renewed as soon as it loses its elasticity, and the hamper must be kept in good repair.

*Loading: Full Loads.*—All carboy-hampers to be tied together, any space remaining at end or side of wagon to be filled tightly with suitable packing. *Small consignments.* Carboy-hampers to be tied together, the carboys to be loaded at one end of the wagon, and secured there, either by a retaining bar, or by tying the carboy-hampers to the wagon-ends with rope.

In view of the large number of carboys broken in transit, chemicals in carboys must not be loaded on the top of other goods, or in the same wagon with goods named in the foregoing paragraph, or any other goods liable to be damaged in the event of the breakage, or leakage of the contents of the carboys.

All carboys must be securely bunged or stoppered and luted, except when containing hydrochloric acid, in which case tightly fitting straw-bungs may be used, if they be securely tied over with string.

The rules concerning nitric acid packages are given *suprà*, p. 258.

*Tank-wagons.*—When supplying large consumers, and especially when sending great distances by land, glass carboys are not now employed for the carriage of sulphuric acid. For some time leaden or copper vessels were used for this purpose, but these have been abandoned for *wrought-iron vessels*, more especially *tank-wagons*. Balmain & Menzies patented in 1869 this way of carrying sulphuric acid, which, however, seems to have been previously in use locally; its general use appears to date from 1880. The stronger the acid the less danger is there

or any action upon the iron; but even down to  $130^{\circ}$  Tw. it can be safely carried in iron, provided there are no injurious impurities present, such as nitrous acid, and that the air has no access—the latter, because its moisture condenses on the surface of the acid, forms a layer of dilute acid, and corrodes the iron in that place.

The iron acid-tanks are sometimes made of an angular section, like ordinary railway-trucks; but these have been almost entirely superseded by cylindrical boiler-shaped tanks of 10 tons' capacity. A great advantage of the latter is, that they resist pressure, and that, at the consumer's works, they can be fitted with an arrangement for forcing the acid out of them into a store-tank on the premises, so that the tank-wagons are at once emptied and can be sent back to the seller's works. Smaller tanks of this kind, say holding 2 or  $2\frac{1}{2}$  tons, can be used for road-traffic.

Nörrenberg (*Chem. Ind.*, 1896, p. 553) gives special instructions for cleaning out tank-wagons used for sulphuric acid.

Iron tank-wagons can be used for concentrated acid as well as for chamber-acid. The thickness of the plate for acid down to  $140^{\circ}$  Tw. is generally  $\frac{3}{8}$  to  $\frac{1}{2}$  in., for chamber-acid  $\frac{5}{16}$  in. The plates must be very well riveted together and tightly caulked, as any leakage of acid will cause a strong corrosion on the outside, in spite of the self-evident precaution of keeping the iron very well painted with coal-tar varnish. For the same reason the tanks, when empty, must be kept tightly closed; any part temporarily exposed to the air, e.g. manholes, etc., should be covered with sheet-lead.

The emptying takes place by means of a siphon, or else by an angular valve-tap as shown in Fig. 474, or by an india-rubber hose closed by a strong clamp. India-rubber, however, should be employed only for chamber-acid. The valve is made of gun-metal (ordinary, not phosphorous bronze, which does not resist the acid so well); the iron spindle is cased

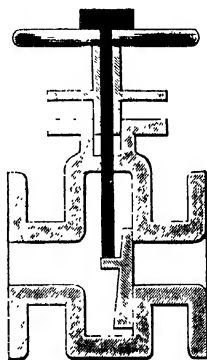


FIG. 474.

with hard lead up to the screw-thread, the stuffing-box is packed with asbestos.

In spite of all precautions, a little gas is generally evolved in acid tank-wagons made of iron, which, in opening them, may cause some acid to splash about and injure the men. This is avoided by a contrivance constructed by Vorster and Grüneberg (Oppler, *Chem. Ind.*, 1889, p. 528). On the top of the boiler-tank there is a pipe, and within this another pipe, closed at bottom and open at the top. The annular space thus formed is closed at top and open at bottom. The inner pipe has two lateral openings near its bottom; through these the gas collected in the boiler-tank gets into the inner pipe and thence escapes outside, whilst the acid carried along collects in the annular space between the pipes and runs back again.

Pfeffer (*Z. angew. Chem.*, 1908, pp. 98 to 104) discusses tank-wagons for acids in detail. Square tanks on these wagons are more easily placed on wheels and more stable than cylindrical tanks, but in every other respect cylindrical tanks are to be preferred. The experience gained in the construction of steam boilers comes in very usefully here. Cylindrical tanks are cheaper than square ones; the ends are more easily put on; they are more easily and quickly emptied, and more easily cleaned. The way of putting them on the wheels is described in detail. They are filled through the dome, in which there is an air-hole, covered with fine-meshed wire-gauze in order to prevent explosions by a fortuitous taking fire of the mixture of air and gases over the acids. Directly underneath the charging-hole is the discharge-pipe, which is divided into two branches, each of them provided with a tap; there is also a shutting-off valve inside the cylinder, the spindle of which comes out at the dome. Sometimes diaphragms are provided in the cylinder, in order to prevent excessive oscillations of the acid in shunting, etc. (see below). The production of the iron against the acid may be effected by a lead lining, but ebonite is preferable for this purpose.

*Acid-boats.*—Where the acid has to be carried on canals, the boats may be arranged as tanks by lining them with lead (which in such cases is much more suitable than for railway carriage) or even with iron. As was shown by Kuhlmann, jun., in 1878 (*Chem. Ind.*, 1879, p. 333), such boats when used for this purpose

are subject to dangerous shiftings of the centre of gravity by the oscillations of the acid; but this is entirely prevented by providing longitudinal partitions, leaving an air-space widening out at the top, as shown in Fig. 475.

Holden (B. P. 3805 of 1877) proposes to construct acid-tanks from wood which has previously been warmed and soaked with paraffin. The edges are to be made tight by a solution of gutta-percha in naphtha.

For *sea-transport* wooden boxes lined with lead are usually employed; iron would probably answer better.

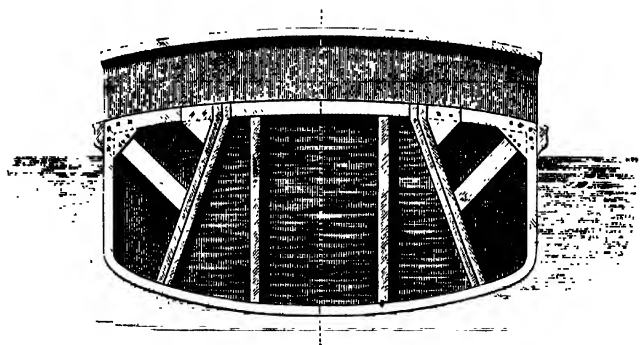


FIG. 475.

Vorster and Grüneberg (Ger. P. 24748) proposed the following plan, especially with a view to sea-carriage:—Dry and finely divided *kieselguhr* (infusorial earth) is saturated with three or four times its weight of strong sulphuric acid. The product, which contains at least 75 per cent. of acid, retains its pulverulent form and can be transported by land or sea in lead-coated sheet-iron vessels without any risk of breakage. When it reaches its destination the mass is either used directly or is diluted with water, and the acid is separated from the *kieselguhr*. [This plan has not been found very practical, nor does it seem to be called for, as the pure (liquid) acid itself can be sent out perfectly well in sheet-iron vessels closed by screw-plugs.]

White and Rickman (B. P. 17095 of 1887) for a similar purpose mix sulphuric acid with anhydrous sodium or



magnesium sulphate (hydrochloric acid with calcium or magnesium chloride), dissolving the salt in the acid by the action of heat, and allowing it to solidify on cooling. The salt frequently does not interfere with the use of the acid. This plan is evidently not practical.

"Special steel casks for strong sulphuric acid," ranging from a capacity of 20 to 450 gallons, of barrel shape, are manufactured by The Steel Barrel Company, Ltd., Phoenix Wharf, Uxbridge.

## CHAPTER X

### ARRANGEMENT OF A SULPHURIC-ACID WORKS ON THE CHAMBER PLAN ; YIELDS AND COSTS

ALTHOUGH it is obvious that no fixed rules can be laid down as to the way in which a sulphuric-acid factory should be planned, yet a few remarks upon this subject may be of some use. In the first place, the arrangement of acid-works depends upon whether they are to supply only chamber-acid or acid up to, at most, 150° Tw., or rectified O.V. The first case, which is that of fertiliser-works, and even of some salt-decomposing works, is, of course, the simplest, no concentrating-apparatus whatever being required. Formerly such works usually did not possess any, or only small, Gay-Lussac or Glover towers. But although the latter in this case are not called upon to furnish a larger quantity of strong acid than is needed for the Gay-Lussac tower, and although they do furnish much more than that, yet water has sometimes to be used in order to bring the acid down to the strength required; but it is most irrational, in view of the waste of water, the yield of acid, and even the nuisance produced by noxious vapours, to work without any or without fully efficient Glover and Gay-Lussac towers.

Where acid concentrated up to 140° or 150° Tw., but of no special degree of purity, is required (that is, generally in works decomposing salt and for a few other purposes), it is easy to obtain the whole of the acid of that strength without any special concentrating-apparatus, by means of Glover towers. Where, however, purer acid has to be made, either for sale or for further concentration in glass or platinum, concentrating-pans must be provided. These may be heated either by the heat of the brimstone- or pyrites-burners, and they are then of course placed over these or else over the flue conveying the

kiln-gases to the Glover tower; in either case no separate ground-space is required for them.

Or else (which we deem unnecessary in all ordinary cases) they are heated by special fires, either from the top or from the bottom, or by steam. Most frequently room will be found for this under the acid-chambers or immediately adjoining.

Finally, where rectified oil of vitriol is made, this can be (and in many cases is) done underneath the chambers; but more usually, especially in the case of glass retorts; a special retort-house is constructed for this purpose.

Without taking any further notice of the last concentration of the sulphuric acid, we make the following remarks on the arrangement of the remaining apparatus. The lowest level is always occupied by the pyrites- (or brimstone-) burners; only there must be space left for wheeling away the cinders. Accordingly the burners are always erected on the ground-level; and the stone-breakers, if present, are mostly placed on the same level. The pyrites in large works arrives on a railway resting on trestles (gears) and is tipped between the trestles, in order to be taken away as it is wanted, to be broken and laid in front of the kilns. Where the supply of ore is quite regular, the stone-breaker can be disposed so that the ore will pass direct from the railway-trucks through the breaker, and arrive broken on the ground-level, thus saving labour. Where the ore is broken by hand, or where it arrives in large and irregular parcels, this cannot be done very well.

• Unbroken pyrites, especially non-cupreous, can be stored in the open air without much damage; but after breaking it should be protected from the rain. It is sifted directly after the dust is stored apart from the lumps; and both are taken to the burners across a weighing-machine. • The breaking, sifting, and storing of the broken pyrites, nearly always takes place underneath the chambers. Where these are high enough above the ground, the burners themselves can be placed beneath them; otherwise they are erected in a separate shed immediately adjoining, and it is advisable to take this course even in the former case. Any cooling-pipes or tunnels are arranged along the side or on the top of the chambers. Where the burners are built under the chambers, the outer pillars of

these must be connected by a light open-work wall, to keep the wind off the burners.

The nitre-ovens, where such are provided, are always built at the end of each set of burners and as a continuation of it.

The steam-boilers are also sometimes placed under the chambers; but it is decidedly better to put them in a shed outside, both in order not to injure the timber of the chamber-bottom by steam leaking or blowing out of the safety-valves, and to save the boiler-plate from being corroded by any accidental droppings of acid. In case of an explosion the damage will then not be quite so serious as if the boilers stood directly underneath the chambers.

As the burners are built on the ground-level, as the chambers are in any case erected at a certain height above it, and as the gas-pipe also enters into the upper part of the chamber, the gas-pipe must necessarily rise a good deal; and the conditions of draught are thus satisfied.

If, however, a Glover tower is to be used, it must be placed between the burners and the chambers. Formerly a few burners were sometimes set aside for working the nitre-ovens by their heat and taking the nitre-gas direct into the first chambers; this is now rarely or never done, but each set of burners is followed by the nitre-ovens and then by the Glover tower. Where liquid nitric acid is employed, the nitre-oven is simply left out. The Glover tower itself must be placed with its base rather higher than the top of the gas-flue over the burners. In this way the burner-gas can travel horizontally to the tower; but it is generally made to rise a little higher and to descend slightly into the tower, so that any acid splashing into the pipe runs back into the tower. Usually the levels of the Glover tower and the chamber are planned in such a way that the gas issuing from the tower can still enter the chamber below its top. This secures good draught into the chambers, provided there is a sufficiently strong pull at the exit end. Where this is not the case, the indispensable draught in the pyrites-burners is sometimes brought about by taking the gas up a high Glover tower, or else upwards from the tower through a special pipe, and then down again through the chamber-top (cf. p. 911). In some cases injectors or fan-blasts are made to produce the necessary draught (p. 753).

On the other hand, the chambers are sometimes placed so high that the top of the Glover tower is below their bottom, and the chamber-acid can be run directly into the tower.

The chambers, as already mentioned, are either arranged so that their floors are all at the same level, or so that each following chamber is from 1 to 3 in. higher than the preceding one. A greater difference is not necessary, but is sometimes employed for local reasons. From the last chamber issues a pipe connecting it with the Gay-Lussac tower, which can only exceptionally be placed on a foundation so elevated that this pipe need not descend—certainly a preferable arrangement if the levels permit it. Provision must also be made for interposing a long cooling-channel between the last chamber and the Gay-Lussac tower, unless there is a special small chamber provided for cooling and drying the gas, which chamber receives no steam.

In any case the Gay-Lussac and Glover towers should be combined into a set, with the necessary tanks, air-pump, acid-eggs, etc., arranged at the foot, by which the attendance will be much facilitated. In large works with several sets of chambers it is preferred rather to combine several Glover towers, and in any case several Gay-Lussac towers, to form a set.

In the previous editions of this book drawings of a set of chambers with appurtenances were given to serve as a general guide for the observation of the just-mentioned rules. Not to speak of the first edition, even the drawings contained in the second edition are somewhat out of date now. Fortunately I am enabled, by the kindness of Mr Niedenhihr, to show modern plans for two separate cases, drawn expressly for this book. The first case (Figs. 476 to 479) is that of works on the old and hitherto most general style, where no special means are employed for diminishing the chamber-space. The plans show how such chambers and their belongings can be most suitably built in a climate where they must be enclosed in buildings. In England this is usually not done, but the alterations to be introduced in the latter case are easily understood (*cf.* p. 616).

On the necessarily adopted small scale most details of construction and auxiliary apparatus cannot be shown, and for these we must refer to Chapter V., where also the details

of the French (p. 608) and American systems (p. 611) will be found.

The plant shown here is intended for the production of 20 tons real monohydrated  $\text{H}_2\text{SO}_4$  per twenty-four hours, in the shape of the corresponding amount of chamber-acid. This is a somewhat large set, but Mr Niedenfuhr considers it best to work on such a scale, if all modern improvements are applied. Since all dimensions are given (in metrical measure), the reduction to a smaller size can be easily made, where such is required.

$A_1 \dots A_{12}$  are twelve pyrites-burners for pyrites in pieces. The burner-gases pass through the flue-dust chambers B, an ascending gas-flue C, and a cast-iron pipe D, lined with fire-brick, into the Glover tower E, and from this by pipes  $F_1$  and  $F_2$  into the first chamber  $G_1$  in its upper part. They leave this chamber on the opposite side near the bottom through three pipes  $H_1, H_2, H_3$ , connected with a common pipe H, which ascends and introduces the gases into the second chamber  $G_2$  near its top through pipes  $H_4, H_5, H_6$ . In the same way the gases issue from  $G_2$ , through  $I_1, I_2, I_3$ , ascends through I, and enter through  $I_4, I_5, I_6$ , into the third chamber  $G_3$ . The object of dividing the gases among three inlet- and outlet-pipes is to utilise the whole section of the chamber for the process and to avoid any dead corners.

From the third chamber the gases travel through the long pipe K, where they are cooled and dried, into the Gay-Lussac towers. At the lowest point of K the condensing water is discharged. The gases pass seriatim through the two towers  $L_1$  and  $L_2$  and issue from the latter into the atmosphere, unless it is preferred to pass them into a chimney, or, preferably, to draw them out by mechanical means.

The total cubic space of the chambers is about 310,000 cub. ft., which, according to the experience with ordinary chambers at the majority of German works, is required for the regular daily production of 20 tons  $\text{H}_2\text{SO}_4$  in the shape of chamber-acid. [This is as nearly as possible = 19 cub. ft. per lb. of sulphur burned, and corresponds with the practice of the majority of English works; but much less space is required for the "intense" or "high-pressure" style of work, cf. pp. 639 *et seq.*]

The Glover tower in its lower half is packed with a network

## 1232 ARRANGEMENT OF A SULPHURIC-ACID WORKS

of bricks on edge, in its upper half with dishes. The first Gay-Lussac is packed with dishes, the second with coke.

Fig. 476 is a plan of the whole plant, the store-tanks below the chambers and above the towers being marked in dotted lines. Fig. 477 is a sectional elevation on the line A—B, through the dust-chamber, Glover tower, and first acid-chamber; Fig. 478 is a sectional elevation C—D, through the pyrites-burners, showing one of the Gay-Lussacs and chamber  $G_3$  in front elevation. Fig. 479 is a sectional elevation on line E—F through the chamber building.

The building for the vitriol-chambers is planned in an economical way, proved to be both cheap and efficient at the various works of the Rhenania Company. The chambers rest on brick pillars of such strength that they can be reduced to a small number, and thus permit of properly utilising the space below the chambers for various purposes. The space round the chambers themselves is cased in wood, and the roof is covered with roofing-felt, with a ventilating rider.

The plans do not show the steam-boilers; it is understood that the steam comes from a central plant through the 2-in. pipe M (Figs. 476 and 477), from which branches  $M_1 \dots M_{10}$   $\frac{7}{8}$  in. wide inside carry the steam to the centre of the chamber-top. The ascending part of the steam-pipe is provided with a trap for the condensing water in its lowest point; the mains M above the chambers descend slightly towards the pipes  $M_{11}$  and  $M_{12}$ , which carry away the condensed water. [Cf. on feeding the chambers with water in the shape of spray, pp. 728 *et seq.*]

The Glover tower is served by two acid-tanks  $R_1$  and  $R_2$ , placed on its top, for nitrous vitriol and chamber-acid (from  $G_3$ ). At its bottom the acid runs through two coolers  $S_1$  and  $S_2$  into tank  $R_6$ , from which it is lifted by pulsometer  $P_1$  into tank  $R_4$ , which supplies the Gay-Lussac tower  $L_2$ . The weak nitrous vitriol issuing from the latter runs into  $R_8$  and is lifted by pulsometer  $P_2$  into  $R_3$ , in order to be enriched in tower  $L_1$ . From this it runs into  $R_7$  and is pumped by pulsometer  $P_3$  into  $R_1$ , serving for the Glover tower.  $R_2$ , on the same tower receives acid from chamber  $G_3$  through pulsometer  $P_4$ .

Mr Nidenführ has also furnished the following estimate of cost, based on his practical experience and on German prices

## COMBINATION OF CHAMBERS AND TOWERS 1233

in 1902. I translate his figures into English measures and money:—

I. <i>Ground-space</i> , 27,000 superficial feet . . . . .	£2,500
II. <i>Building</i> , for burners 3770 superficial feet . . . . .	£420
" for chambers, 14,500 superficial feet, including brick pillars, wood casing for chambers, felt roof and chamber frame . . . . .	2,960
Foundations and frames of towers . . . . .	120
Sundries, including boiler-shed . . . . .	300
	<hr/> 3,800
III. <i>Steam-boilers and machinery</i> —	
Steam-boilers 430 superficial feet heating surface, including brickwork, etc. . . . .	300
Air- and water-pumps . . . . .	120
Pipes for steam, air, and water . . . . .	125
Pulsometers, including erection and acid-pipes . . . . .	205
	<hr/> 750
IV. <i>Pyrites-burners</i> —	
12 lump-burners . . . . .	900
Dust-chambers, nitre-ovens, connection with Glover-tower . . . . .	225
	<hr/> 1,125
V. <i>Chambers and towers</i> —	
240 tons lead, at 16s. 6d. per cwt., including cost of burning and materials for same . . . . .	3,900
Materials for packing Glover tower, etc. . . . .	300
" " Gay-Lussac towers . . . . .	475
Sundries . . . . .	325
	<hr/> 5,000
VI. <i>Sundries (reserve)</i> . . . . .	1,325
	<hr/> £14,500

For the *second* case (as explained, pp. 668 *et seq.*), Figs. 480 to 485 give sketches of a set of chambers designed by Mr H. H. Nidenführ, as embodying the *later progress in the combination of chambers and towers*. This set is to suffice for burning 20 tons 48 to 50 per cent. pyrites in twenty-four hours. The pyrites is burned in Herreshoff furnaces, *a*, *a* (*cf.* p. 482), or in any other kind of pyrites-kiln or burner. The gases first pass through the dust-chamber *b*, *b*, then through the Glover tower *c*, into the lead chamber *d*, provided with air-cooling shafts (p. 653) and water-spray injectors (pp. 728 *et seq.*). From here they pass through plate-tower *e*, containing 10 layers of 28



## 1234 ARRANGEMENT OF A SULPHURIC-ACID WORKS

plates each, at a distance of 12 in. from layer to layer, then into another lead chamber *f*, followed by plate-tower *g*, with 10 layers of 24 plates each, 12 in. apart, and plate-tower *h*, with 12 layers of 24 plates 12 in. apart; at last at the top into plate-tower *i*, containing 16 layers of 20 plates each, 8 in. distant. This tower they leave at the bottom by the long conduit *k*, which takes them to the first Gay-Lussac tower, containing 24 layers of 16 plates each, 4 in. distant; and this is followed by the coke Gay-Lussac tower *m*, a fan-blast being placed between these two towers.

The circulation of the acids is marked by arrows, but it is more clearly shown in Fig. 485. The acid from the Glover tower *c* runs through an air- and water-cooler into tank  $R_1$ . A pulsometer, *P*, pumps it into tank  $R_6$ , fixed above the coke Gay-Lussac tower *m*. From this the acid runs to the bottom into tank  $R_2$ , is pumped by pulsometer  $P_1$  to  $R_7$  above the plate Gay-Lussac tower, runs from this into tank  $R_3$  and is pumped into tank  $R_8$  above the Glover tower. The chamber-acid is run into tank  $R_5$  and is pumped partly into  $R_9$  above the Glover tower, partly into  $R_{10}$  above plate-towers *g*, *h*, *i*. From there the acid runs into tank  $R_4$ , is pumped into  $R_{11}$  above plate-tower *e*, and runs from this into the chamber.

Mr Nicdenführ calculates the work to be done by this set as follows:—

	$H_2SO_4$ kg.
Chamber <i>d</i> = 1819 cub. met. at 4 kg. $H_2SO_4$	= 7,276
Plate-tower <i>e</i> = 280 plates „ $12\frac{1}{2}$ „	= 3,500
Chamber <i>f</i> = 1516 cub. met. „ 2 „	= 3,032
Plate-tower <i>g</i> = 240 plates „ 8 „	= 1,920
„ <i>h</i> = 288 „ „ $4\frac{1}{2}$ „	= 1,296
„ <i>i</i> = 320 „ „ 2 „	= 640
Production of Gay-Lussac and Glover towers	= 2,336
	<hr/>
	20,000

The cost of this plant is given later on. The statements of Lütj (Z. angew. Chem., 1897, p. 489) have consequently become obsolete.

The comparative calculations of the cost of plant for ordinary and for "high pressure" style of work, by Nemes, have been given *suprà*, p. 644.

*Cost of Chamber-plant in France.*

Sorel gives the following figures as the actual cost-price of apparatus at l'Oseraie (France), apart from the value of land—

1. Buildings—	Francs.	cent.
Chamber-sheds (all brickwork) . . . . .	50,700	90
Furnace-shed „ . . . . .	15,147	15
Steam-boiler shed „ . . . . .	9,269	10
Foundations and timber-work for Glover and Gay-Lussac	14,604	35
Main flue . . . . .	3,940	55
Chimney (2 m. inside, 40 m. high) . . . . .	13,088	35
	106,750	40
2. Apparatus—		
Pyrites-burners . . . . .	31,686	70
Glover tower . . . . .	26,188	75
Chambers (4500 cubic metres—nearly 160,000 cubic feet)	74,131	80
2 Gay-Lussacs, 20 m. high . . . . .	22,804	10
Exit-gas tube . . . . .	6,157	15
Steam-pipes . . . . .	4,541	25
Acid-tanks and acid-eggs . . . . .	15,144	55
Tools . . . . .	943	05
	181,597	35
3. Steam-boilers and engines—		
2 steam-boilers and setting . . . . .	21,267	60
1 air-pump and pipes . . . . .	9,167	15
1 water-pump and pipes . . . . .	7,114	55
1 fan-blast and driving-engine . . . . .	3,192	50
	40,741	80
Grand total . . . . .	229,089	55

This apparatus is capable of making 6000 tons of O.V. per annum with the “forced work” or “high-pressure style” frequently alluded to, viz., a chamber-space of only 11 or 12 cub. ft. per lb. of sulphur burnt. This is made possible by the extraordinarily great size (and cost) of the nitre-recovery apparatus. If this had been made of the usual dimensions, the cost would have been about 38,000 francs less, but then the production, at the usual rate of 2.25 kg. per cubic metre (say about 21 cub. ft. per lb. of sulphur), would have been only 3600 tons per annum.

On the arrangement of sulphuric-acid works in the United

States interesting notes are contained in the papers of Falding (*Min. Ind.*, viii. p. 579, and ix. p. 617) and of Gilchrist (*J. Soc. Chem. Ind.*, 1899, p. 459).

#### YIELDS AND COSTS OF SULPHURIC-ACID MANUFACTURE.

In calculating the cost of manufacturing sulphuric acid, we must take into account the following factors:—

- Cost of sulphur (brimstone, pyrites, blende);
- Consumption of nitrate;
- Consumption of fuel;
- Wages;
- Wear and tear of apparatus;
- Interest on capital, general expenses, etc.;
- Yield of sulphuric acid.

We will, in the first place, inquire into the *consumption of nitre* and the *yield*. We are here met at the outset by the difficulty of comparing the statements from different sources, arising from different fundamental quantities being taken as the basis of the calculation. Some calculate all the sulphur contained in the charge, others only that portion which has actually been burnt, not taking into account the sulphur left in the cinders. The latter way of calculating is more rational in theory; but in practice it is often less useful than the former. For it is known with perfect accuracy how much pyrites, and how much sulphur contained in it, has been put into the burners; but as the percentage of sulphur in the cinders varies, it is not known precisely how much has been burnt. Besides, the question is not only how the chamber process itself works, but also how the burning has been done, on which the smaller or larger residue of sulphur in the cinders depends. It is another case when the percentage of sulphur in the cinders is almost constant and altogether very slight, as in burning pure ores in shelf-burners; in this case it is indifferent which way of stating the results is adopted.

The *consumption of nitre* is stated sometimes in percentages of pure sodium nitrate, sometimes in percentages of commercial nitrate; and in the latter case either 95, 96, or 97 per cent. is assumed. Here also we have a source of uncertainty and divergence, although not of such importance as that just

mentioned. To each part of sodium nitrate correspond 63.53 parts of  $N_2O_5$  or 74.12 parts of  $NO_3H$  or 134.76 of nitric acid of 1.34 sp. gr. (at  $15^\circ C.$ ), the strength usually employed in vitriol-works.

The worst confusion prevails regarding the calculation of the *yield of sulphuric acid*. Some state it in terms of chamber-acid of  $50^\circ B\acute{e}$ . ( $=106^\circ Tw.$ ), some as  $60^\circ B\acute{e}$ . ( $=144^\circ Tw.$ ), some as commercial  $168^\circ Tw.$  ( $=66^\circ B\acute{e}$ ), some as real monohydrate; what is worse, the reduction upon these terms is made by very varying and, in part, quite erroneous tables (*cf.* p. 295); and frequently it is quite uncertain whether by "oil of vitriol" (O.V.) an acid of 93 to 94, or one of 96 to 98, or one of 100 per cent.  $SO_4H_2$  is meant. In the following pages, so far as the sources permit, all statements will be reduced to the only rational term, that of monohydrate,  $SO_4H_2$ .

Frequently, at works where none of the sulphuric acid is sold, but the whole is used for making salt-cake, the yield is calculated indirectly, from the quantity of common salt decomposed by it, according to more or less arbitrary assumptions regarding the quantity of sulphuric acid consumed for decomposing a unit of salt. Thus several large manufacturers, working with open roasters, assume a consumption (and consequently a make) of 81.33 parts of  $SO_4H_2$  to each 100 parts of common salt. Now, in muffle-furnaces (blind roasters) decidedly less sulphuric acid is consumed than in open roasters; and yet a large Alsatian maker, using blind roasters only, assumes a consumption of 74 per cent. of vitriol of  $66^\circ B\acute{e}$ . on the sulphate,  $=85.8$  per cent. on the salt, or 80.8 per cent. of real  $SO_4H_2$  on the salt, which is all but equal to the above-named figure. This proves the uncertainty of such bases of calculation.

Consistently, several English alkali-works have given up calculating the yield of sulphuric acid altogether; they only state the yield of salt-cake upon the pyrites burnt, or upon the sulphur contained therein. Of course, this way of calculating is only possible where no acid is sold or used for any other purpose than decomposing salt.

Often no mention is made whether that portion of the sulphuric acid employed for the *decomposition of nitre*, which leaves the factory in the shape of acid sulphate (nitre-cake), has

been allowed for in the calculation. We specify this in the following accounts, wherever it can be done from the sources.

Of course the following enumeration does not contain all and every statement of the kind scattered in innumerable publications, but only so much as suffices for forming a good idea of the state of affairs, both in former and in recent times.

### I. CONSUMPTION OF NITRE.

(Cf. also the statements, pp. 637, 640, 643.)

#### 1. For Brimstone-acid.

##### (a) Without Recovery of the Nitre-gas.

For 100 parts of brimstone charged :—6 to 9 parts (Knapp, *Chem. Technol.*, 1866, i. pp. 2, 298); at least 6, sometimes  $7\frac{1}{2}$  parts (Schwarzenberg, *loc. cit.* p. 400); 6 to 8 parts (Payen, *Précis*, 1877, i. p. 322); 7 to 8 parts (Scheurer-Kestner, in Wurtz's *Dict. de Chim.*, iii. p. 158); 8.9 parts (Stevenson and Williamson, in Richardson and Watt's *Chem. Technol.*, iii. p. 318); 10 parts (Wright, *Chem. News*, xvi. p. 93). Most of the sulphur-burning works enumerated in the Official Alkali Report for 1885 consumed 9 or 10 parts.

##### (b) Recovering the Nitre-gas.

Four to 5 parts (Knapp, *loc. cit.*); 3 parts (Schwarzenberg, *loc. cit.* p. 401); 5 parts (Payen, *loc. cit.* p. 322); 3 to 4 (Scheurer-Kestner, *loc. cit.*); 3 parts (several American works visited by myself in 1895).

#### 2. For Pyrites-acid.

##### (a) Without Recovery of Nitre.

At the Oker Works in 1857, 14.4 parts; 1859 to 1863, 13.4 for 300 parts strong acid (Knapp, Kerl-Stohmann); for 100 sulphur charged in the shape of pyrites, 10 parts (Schwarzenberg, *loc. cit.* p. 432), 9, to 11 parts (Payen), 12 to 14 parts (Scheurer-Kestner). According to Wright (*loc. cit.*), in different works, with pyrites of 45 to 50 per cent. 8.5 parts, of 30 to 50 per cent. 10 to 12 parts, of 35 per cent. 12.5 parts; with a set of chambers in

bad repair, in the first year 9.31, in the second 9.84, in the third 10.02 parts. According to Gossage (*ap. Richardson and Watts*, p. 317) 13.3 parts with 30 per cent. Irish pyrites. From my own experience, on an average, with pyrites of 40 to 44 per cent. 10.8 parts; in neighbouring works 10.5 parts with smalls, 9.4 with lumps. At some French works I was informed of a consumption of 1.5 to 1.97 kg. nitre per 100 kg. acid of 50° Bé., equivalent to 2.9 to 3.8 kg. per 100 kg. pyrites of 44.4 per cent., or 6.5 to 8.5 kg. per 100 kg. of the sulphur contained therein. [This statement does not appear trustworthy, viz., too low, looking at the figures from the same source for working with a Gay-Lussac tower.] Naville's statements see below.

(b) *Recovering the Nitre-gas.*

For 100 sulphur in the pyrites:—5 parts (Schwarzenberg, *loc. cit.* p. 432); 7 parts (Payen, *loc. cit.* p. 322); 7 to 8 parts, less with higher towers (Scheurer-Kestner, *loc. cit.*); 3.8 parts (Glover). According to my own experience (with insufficient absorbing-space) 3.5 to 4.5 parts; but when the work was irregular, chambers out of repair, as much as 6 or even 7 parts. Neighbouring large works 3.5 parts. K. Walter guarantees 0.7 part of nitre to 100 parts acid of 66° Bé. = 2.04 parts to 100 sulphur in 44 per cent. pyrites. At the Oker works in 1877, 3.75 to 4.5 parts per 100 sulphur were used with pyrites pretty rich in sulphur, 4.5 to 6 parts with mixed and galeniferous ores; in 1901 on the average 4.8 parts. In French works (same source as above), they use per 100 kg. acid of 50° Bé. 0.9 to 1.24 kg., per 100 pyrites 1.73 to 2.38, per 100 sulphur charged 3.85 to 5.37 kg. of nitre. According to notes collected by myself in 1878:—In German works, 2.3 to 3.1 nitre per 100 sulphur; in the best English works, about 3 per cent. (exceptionally, as stated by Affleck, 2.2 per cent.; in Lancashire some large works use even 5 per cent., cf. the table on p. 637); in French works (with a Glover tower), 2.7 parts, (without) 4.2 to 4.7 parts to 100 sulphur charged.

The consumption of nitre is always less in winter than in summer. As between nitric acid and solid nitre no difference worth mentioning can be established; if anything, slightly less nitre is used in the solid form than as nitric acid, if not the

acid itself, but the nitre from which it was originally made is taken as the basis of calculation, as it ought to be.

Notes recently collected :—English works 2.5 to 3.5 per cent. At one works they asserted that the actual loss was only 15 lb. nitre per ton of pyrites, that is, less than 1.5 per cent. on the sulphur, with only 17 cub. ft. chamber-space, and a yield of  $41\frac{1}{2}$  cwt. 96 per cent. salt-cake.

A first-class German works with specially good absorbing-apparatus and 16 cub. ft. chamber-space :—1.8 to 2.2 per cent.  $\text{NaNO}_3$  on sulphur burnt.

Pierron (*Monit. Scient.*, 1900, p. 567) states as the consumption of nitre in France = 0.75 to 1.12 kg. per 100  $\text{H}_2\text{SO}_4$  (= 2.25 to 3.36 kg.  $\text{NaNO}_3$  per 100 S) for pyrites; and 1.0 kg. for 100  $\text{H}_2\text{SO}_4$  with blende.

Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1334) states the consumption of nitre in ordinary chamber plants with good Glover and Gay-Lussac towers to be now frequently = 0.75 for 100 parts  $\text{H}_2\text{SO}_4$ ; with Meyer's chambers (p. 622) only = 0.60.

In America, according to Falding and Gilchrist (1901), about 1.05 nitre for 100  $\text{H}_2\text{SO}_4$  is the rule.

## (II. YIELD OF SULPHURIC ACID, CALCULATED AS $\text{SO}_4\text{H}_2$ .)

(Theoretically 306.25 parts per 100 sulphur.)

1st. *From brimstone* (always upon the sulphur actually burnt) 290 to 300, on the average 296 (Knapp); 297  $\text{SO}_4\text{H}_2$  = 319.35 acid of 66° Bé. (Schwarzenberg); "usually 296 to 300; even the theoretical quantity has been obtained" (*sic!* Payen, i. p. 321); 290 to 300 (Scheurer-Kestner). At some American works visited by myself in 1890 the yield of acid was stated = 305 real  $\text{H}_2\text{SO}_4$ , which must be an error, attributable to wrong specific-gravity tables, etc.

2nd. *From pyrites.* At Oker, in 1857, 1 cwt. acid of 66° Bé. per 1.89 cwt. ore (Knapp); 1859-1863, per 1.729 cwt. ore (Kerl-Stohmann); 1877, in the same place, 160 chamber-acid of 50° Bé. (106° Tw.) were obtained from 100 pyrites; from 100 rich copper-ores 140 to 150 parts of chamber-acid, from 100 "mixed-ores" 90, from 100 ore mixed with galena 70 parts of chamber-

acid. The residual sulphur in the cinders from pyrites (always containing galena) amounts to 6 per cent., from the other ores 10 to 12 per cent. (Bräuning).

In four Belgian works, 1854 (*Official Report*), on 100 parts sulphur in the pyrites charged 242, 237, 259, 238 parts  $\text{SO}_4\text{H}_2$ . The same works in 1874 by improved arrangement had arrived at 87.81, 92.17, 85.50, 89.30 per cent. of the theoretical quantity, or 268.8, 282.4, 261.8, 273.5  $\text{SO}_4\text{H}_2$  per 100 S (Chadelon).

In the best French works (Schwarzenberg), on 100 sulphur in the pyrites charged, 259.7  $\text{SO}_4\text{H}_2$ ; on the sulphur really burnt 283.43. Payen (*loc. cit.* p. 322) makes precisely the same statement, with the addition that *usually* from 100 kg. 46 per cent. pyrites 100 to 115 kg. acid are obtained (= 239.1 to 250  $\text{SO}_4\text{H}_2$  per 100 sulphur). According to Scheurer-Kestner (*loc. cit.*) there ought to be the same yield on the really burnt sulphur of pyrites as upon brimstone, viz., 290 to 300 parts. According to Wright, with rich Spanish pyrites 82 to 84 per cent. of the sulphur is obtained as acid; of the loss of 15 to 18 per cent., 4 or 5 per cent. is sulphur left in the cinders, and 12 or 14 per cent. other losses. This means a yield of 251 to 257.25  $\text{SO}_4\text{H}_2$  per 100 sulphur charged (evidently with insufficient chamber-space). An anonymous chemist (in the *Chem. News*, xiv. p. 22) states the yield from 30 per cent. Irish pyrites = 82 to 81.1 per cent. of the theoretical, inclusive of the sulphur in the cinders.

My own experience and reliable statements personally obtained by me from large factories (where, however, the acid made was mostly calculated from the salt decomposed) are as follows:—(a) 238.5  $\text{SO}_4\text{H}_2$  on the sulphur charged, with 40 per cent. small pyrites burnt in muffle-furnaces. (b) 240  $\text{SO}_4\text{H}_2$ , ditto, with 42 per cent. lump ore: both without a Gay-Lussac tower. (c) 263.2 on sulphur charged (own experience), with Gay-Lussac tower, but the work being several times interrupted. (d) 272 to 275 ditto (own experience), with a Glover and a Gay-Lussac tower, the latter not large enough. (e) 276.4 on the sulphur charged, or 301.5 on the sulphur burnt (average result of a large, well-managed factory with Glover and Gay-Lussac towers), (f) a number of notes collected in 1878 from the best German and French works agree most remarkably to a yield of 270



to 272  $\text{SO}_4\text{H}_2$  on the sulphur charged, or 285 to 290 on sulphur burnt. In the warmer climates the yield, even with sufficient chamber-space, is always found somewhat less in summer than in winter, about 3 per cent.

The consumption of coals for chamber-steam is stated = 16.3 kg. per 100 kg.  $\text{SO}_4\text{H}_2$  as the average of eight French factories working without Glover towers; at an English works with Glover tower the coal used for the chambers and the air-pump amounted to 17.5 parts per 100 parts of  $\text{SO}_4\text{H}_2$ . At Stolberg (1902) only 8.5 parts of coal were used for the chambers and air-pump for 100 parts acid of sp. gr. 1.71, or 10.9 parts to 100  $\text{H}_2\text{SO}_4$ . Other statements, partly above, partly below those just mentioned, will be found in the following calculations.

Kienlen (*Monit. Scient.*, 1889, p. 1238) makes the following statements concerning the work done at the best French factories in the year 1889. With good pyrites and properly constructed apparatus, the yield on 100 parts of sulphur *burned* is 295  $\text{H}_2\text{SO}_4$ . One hundred parts of pyrites leave about 68 parts of cinders, with an average percentage of 1 per cent. sulphur. With Sain-Bel ore of 51.5 per cent. S, 100 parts of pyrites will yield  $2.95 \times (51.5 - 0.68) = 140$  parts of monohydrated sulphuric acid, corresponding to a yield of 291  $\text{H}_2\text{SO}_4$  on 100 S, in the pyrites *charged*. There is thus a loss of 15.25  $\text{H}_2\text{SO}_4$ , or 4.97 per cent., the sulphur being used up as follows:—

Recovered in the shape of $\text{H}_2\text{SO}_4$	95.03
Loss in the exit-gases	3.65
Lost in the cinders	1.32
	<hr/> 100.00

The consumption of nitrate of soda in the best works averages 0.90 for 100 monohydrate produced = 1.35 for 100 pyrites, or 2.60 for 100 sulphur charged. This is obtained even with "forced work," where 1 cb.m. of chamber-space is made to yield 3.5 or even 4 kg. of  $\text{H}_2\text{SO}_4$  in twenty-four hours.

I have been favoured by the firm of Ernst Güssefeldt, of Hamburg, with the originals of six years' returns of the acid-works, at Hamburg and at Kastrup (near Copenhagen), with permission to publish the results. The following are the averages taken from the six years' returns (1884-1889)

and they are very good examples of the way of stating the yields:—

*A. Hamburg Works.*

Description of Pyrites: Rio Tinto.

Average quantity burnt per annum	2775.6 tons
„ percentage of sulphur in pyrites	48.8 p. c.
„ quantity of sulphur in pyrites bought.	1354.6 tons
„ „ acid 106° produced	6322.2 „
The same reduced to real $H_2SO_4$	3948.2 „
Sulphur contained in acid produced	1290.0 „
„ lost	64.6 „
Per cent. sulphur lost in cinders <sup>1</sup>	2.69 p. c.
„ „ chamber-process	2.03 „
„ lost altogether	4.71 „
95 per cent. nitrate of soda consumed, total	50.9 tons
Ditto, per cent. of sulphur	3.75 p. c.
Ditto, per cent. of acid 106° Tw.	0.80 „
Real $H_2SO_4$ made per 100 pyrites	142.5 „
„ „ sulphur	291.9 „

*B. Kastrup Works.*

Pyrites burnt per annum (average)	1896.2 tons
Sulphur in pyrites (average)	49.2 p. c.
„ per annum (average)	932.8 tons
Acid 106° produced per annum (average)	4215.2 „
„ calculated into real $H_2SO_4$	2534.5 „
Sulphur contained in acid produced	860.2 „
„ lost altogether	71.9 „
„ lost in cinders	6.85 p. c.
„ lost in chamber-process	0.90 „
„ total	7.75 „
95 per cent. nitrate consumed (average)	22.92 tons
„ per 100 sulphur	2.41 „
„ „ acid 106° Tw.	0.50 „
Real $H_2SO_4$ made per 100 sulphur	282.9 „
Coals used per annum (average)	309.4 „

<sup>1</sup> The quantity of sulphur found in the cinders was from 2.8 to 4; there were 70 cinders assumed per 100 green ore.

The remark is added that the possible errors in stocktaking through inaccuracies of tables and so forth, taking them all as increasing the real yields, cannot possibly in the aggregate amount to more than 4 parts of  $H_2SO_4$  per cent. of sulphur, so that, for instance, the *minimum* quantity really made at the

Hamburg works, in lieu of 291.9, might be 288 per cent. of the sulphur.

*Cause of the Losses in Manufacturing Sulphuric Acid.*

The causes of the loss of nitre have been mentioned in detail, pp. 999 *et seq.* They are (1) loss of nitre-gas carried into the outer air; (2) nitrogen compounds left in the chamber-acid; (3) nitre-gas reduced to  $N_2O$  or  $N$ .

The loss of sulphuric acid itself arises from the following causes:—

1. Incomplete combustion of the sulphur (loss in the cinders); this has also been spoken of before (pp. 446 *et seq.*). With brimstone this loss is but slight; with pyrites it is so much the greater the poorer the ores are, and besides it varies enormously according to the construction of the burners and the care with which they are worked, from 1 to 10 parts and more of sulphur per 100 pyrites, or from 2 to 30 per cent. of the total sulphur. A portion of the sulphur is sublimed, and is found in the connecting-pipes and in the acid itself, and is a clear loss.

2. Losses of  $SO_2$  by leakages of burners, pipes, chambers, etc. By bad draught much loss may occur, since then, at the doors of the burners, nitre-ovens, etc., the gas continually blows outward. Bad pipe-joints, but especially chambers worn down too much, lead to great losses. I have seen chambers which, when ultimately stopped, presented in their interior the image of the starry sky from the innumerable holes in the top; and Wright (*Chem. News*, xvi. p. 93) has independently used the same simile. Many manufacturers have no idea of the great loss which they suffer in this way, by allowing, from motives of ill-timed economy, a chamber to go on too long and trying to patch it up. Wright found in a chamber-system that went three years without repairs:—

	Nitre for 100 parts of sulphur burnt.	Cubic metres of chamber- space per kilog. of sulphur burnt per diem.	Practical yield (theoretical = 100).
First year . . .	9.31	1.150	81.5
Second year . . .	9.84	1.073	75.4
Third year . . .	10.02	1.017	68.4

3. Losses of  $\text{SO}_2$  by *incomplete conversion into sulphuric acid*. Extremely little  $\text{SO}_2$  can remain dissolved in chamber-acid if there is an excess of nitrous compounds present; the greater portion of any remaining  $\text{SO}_2$  escapes from the chambers into the outer air. The reason of this may be irregularity of the process in general, want of nitre, insufficient chamber-space, insufficient draught, etc., as explained in detail previously. The losses from this source are nearly always much greater where the nitre is not recovered, for the reasons stated above. The very widely divergent statements respecting the yield of sulphuric acid are explained to a great extent from this cause alone.

*Statements of Costs for the Manufacture of Sulphuric Acid.*

1. *From Brimstone.*

(Older statements in the second edition, pp. 764 and 765.)

The following cost-sheet for brimstone-acid at an American works has been supplied to me from a thoroughly authentic source; it refers to the year 1888:—

Brimstone, 1,637,127 lb. . . . .	\$19,070-00
Nitre, 91,057 lb. . . . .	1,858-00
Sulphuric acid 60° Bé., 80,380 lb. . . . .	402-00
Labour for operating and repairs . . . . .	2,096-81
Office expenses . . . . .	3,100-00
Coal, 454 tons (at 2240 lb.) . . . . .	463-00
Oil, tools, etc. . . . .	240-00
Repairing materials . . . . .	688-00
Depreciation of buildings, furnaces, and chambers, at 50 cents per ton of acid produced . . . . .	1,721-00
Depreciation of machinery, boilers, etc., at 10 cents . . . . .	344-00
Insurance . . . . .	775-00
Interest (6 per cent. on \$60,000) . . . . .	3,600-00
Ground-rent . . . . .	204-00
	<hr/> \$34,561-81
Sulphuric acid 60° Bé. produced 6,885,373 lb.	
Cost of 100 lb. acid 60° Bé. . . . .	50-2 cents

N.B.—The nitre-cake, having very little value in America, is not taken into account. The consumption of nitre at the above works was unusually high (5 per cent. on the sulphur), owing to the small size of the Gay-Lussac tower.

## 2. From Pyrites.

(Cf. statements referring to former periods in the second edition, pp. 766 *et seq.*)

The following is an altogether authentic account of the cost of making sulphuric acid at a first-class English alkali works for the twelve months ending 31st December 1889.

One ton of real O.V. ( $\text{H}_2\text{SO}_4$ ), in the shape of acid of  $148^\circ \text{Tw.}$ , required on the yearly average:—

	£	s.	d.
14.12 cwt. pyrites, at 11.8s. per ton . . . . .	0	8	4.0
27.06 lb. nitre, at £9, 9s. per ton . . . . .	0	2	3.4
5.30 cwt. coals, at 5s. . . . .	0	1	3.9
Process wages . . . . .	0	3	3.7
Repairs (including wages) . . . . .	0	4	4.1
General expenses and salaries . . . . .	0	2	1.0
Sundries . . . . .	0	1	4.4
	£1	3	0.5

The pyrites used was Spanish ore, testing on an average 49.55 per cent. sulphur. The yield of real  $\text{H}_2\text{SO}_4$  on the sulphur bought was = 286 per cent., on the sulphur burnt = exactly 300 per cent. (calculated by Kolb's table). The chamber-space was rather more than 16 cub. ft. per lb. of sulphur.

Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1334) gives the following cost-account per ton of  $\text{H}_2\text{SO}_4$ , in the shape of chamber-acid with Meyer's chambers (p. 622), intermediate towers, fans, atomised water and other improvements, for a daily production of 20 tons  $\text{H}_2\text{SO}_4$ , with a yield of 300  $\text{H}_2\text{SO}_4$  for 100 S burnt, or 294  $\text{H}_2\text{SO}_4$  for 100 S charged = 147  $\text{H}_2\text{SO}_4$  for 100 pyrites 50 per cent.

	£	s.	d.	
13.605 tons of 50 per cent. pyrites at 4½d. per unit . . . . .	0	12	9	per ton of $\text{H}_2\text{SO}_4$ made
0.160 tons of nitric acid $72^\circ \text{Tw.}$ at 10s. . . . .	0	1	7½	" "
2.800 „ coal at 7s. . . . .	0	0	11½	" "
Labour . . . . .	0	2	10	" "
Repairs and renewals . . . . .	0	2	0.4	" "
Sinking Fund (10 per cent. on plant, 5 per cent. on buildings, etc.) . . . . .	0	3	1½	" "
General expenses, rates, taxes, etc. . . . .	0	2	10½	" "
	£1	6	2	

His calculations further comprise the costs of producing :—

Acid of 94.5 per cent. O.V. concentrated by	£	s.	d.
Kessler's apparatus	.	.	1 9 7
98 per cent. acid by a combined Kessler	.	.	.
and iron apparatus	.	.	1 13 1
98 per cent. acid by a gilt platinum	.	.	.
apparatus	.	.	1 13 3
By the contact process (90 per cent. yield).	1 19 7	with extra	£2 1 5
" " (98 " )	1 18 6	royalty	2 0 4

The cost price of sulphuric acid, made by the ordinary and by the "high-pressure" style of work, as got out by Nemes, has been given *suprà*, p. 645.

For *France*, Sorel gives the following statements concerning the cost price of acid of 50° B $\acute{c}$ . (= 160° Tw.) at l'Oseraie (*cf.* p. 1235), in November 1885 :—

	Quantities.		Price.	Amount.		Total.	
	Total.	Per 100 kg. acid.		Altogether.	Per 100 kg.	Altogether.	Per 100 kg.
	kg.		francs.	francs.	francs.	francs.	francs.
Superintendence	...	...	...	285.00	0.03	1,484.70	0.16
Labour	...	...	...	1,199.70	0.13		
Pyrites	374,550	42.00	26.00	9738.30	1.09	11,191.96	1.25
Nitric acid 36° B $\acute{c}$ .	5,409	0.61	26.58	1455.66	0.16		
Coal	87,850	9.85	21.50	1888.75	0.22	1,888.75	0.22
Lighting	...	...	...	302.20	0.04		
Sundries	...	...	...	30.00	0.04	770.70	0.09
Work of strange machines	...	...	...	438.50	0.05		
Repairs	...	...	...	587.75	0.07	587.75	0.07
General and unforeseen expenses	...	...	...	631.00	0.07		
Deduct :						16,554.86	1.86
Cinders sent out	258,500	28.98	3.00	775.50	0.09	775.50	0.09
Produced 891,821 kil. acid 50° B $\acute{c}$ .						15,779.36	1.77
Equal to 557,388 kil. H $_2$ SO $_4$							2.83

There was produced for 100 kg. 50 per cent. pyrites : 148.81 H $_2$ SO $_4$ .

Commercial nitrate expended per 100 H $_2$ SO $_4$  : 0.74

" " " " 100 pyrites : 1.11.

To the above items of expenditure should be added the amortisation of the plant, the cost of which is detailed on p. 1235, taking the buildings per year at one-twentieth cost price, furnaces, chambers, towers, etc., at one-tenth, steam-boilers and engines at one-fifth cost price; which comes to 31,647 francs per year in all, or 0.527 francs per 100 kg.  $\text{H}_2\text{SO}_4$  for the first four years, 0.39 francs from the fifth to the ninth year, 0.09 francs from the tenth to the twentieth year. (We cannot admit that the amortisation should be calculated at such a low figure from the fifth year onward, as the depreciation of the furnaces, chambers, boilers, etc., must certainly be taken into account, and the "amortisation" should include the sums necessary to provide for their renewal.)

The cost of *concentrated* acid is stated by Sorel as follows, starting from acid of 53° Bé. (= 116° Tw.):—

	Francs
1390 kg. acid of 53° Bé. (= 1490 of 50° Bé.) at f. 20.36	28.31
Sulphate of ammonia, 10 kg. at f. 3.30	3.30
Coal for firing 150 kg. at f. 22	3.30
„ motive power (pumps) at f. 30	0.66
Share of engine work	0.50
Labour	1.60
Repairs	0.60
Amortisation of platinum stills	3.00
General expenses	0.50
Cost of 1000 kg. acid 93 per cent. $\text{H}_2\text{SO}_4$	41.77

This is understood for a production of 9 or 10 tons acid per day in two coupled platinum stills. The amortisation of the buildings is not included.

In *Germany*, F. Curtius (the owner of a large vitriol-works at Duisburg, on the Rhine) discusses at length the cost of sulphuric-acid-making (*Chem. Ind.*, 1879, p. 187). His statements are of great interest, as they refer to old-established works whose produce of vitriol was almost entirely sold as such, whilst other figures frequently refer to works where all general expenses were charged to alkali. The following costs all refer to acid concentrated to 144° Tw. by steam-heat (cf. *suprà*, p. 1098), exclusive of packages and transit. We give only the maxima,

minima, and averages of the fourteen years over which the figures range, viz. 1865 to 1878, in shillings per ton:—

	Minimum.	Maximum.	Average.
(1) Wages . . . . .	5.36	8.48	6.55
(2) General expenses (Management, Insurance, Rates, Taxes, Lighting, Cartage) . . . . .	3.40	4.73	4.23
(3) Office expenses (without commissions, etc.) . . . . .	1.98	2.77	2.32
(4) Repairs . . . . .	3.31	9.31	5.93
(5) Amortisation of plant (4 per cent. on old, 10 per cent. on new plant) . . . . .	2.24	3.72	2.83
(6) Interest on capital . . . . .	3.11	4.25	3.56
Total . . . . .	19.40	33.26	25.42
Extra expenses for new plant . . . . .	...	6.63	1.61
Annual working-days . . . . .	304.4	352.4	329.40

If the acid had to be sent out in glass carboys, which were returned by the buyer, this caused an expense of 4s. to 6s. per ton; but sending it out in copper or lead vessels cost only from 0.6 to 1s. per ton for repairs, etc., of course exclusive of carriage.

Most of the above-stated items appear to be excessively high. As their *bona fides* cannot be doubted, they point to the fact that the process was not carried on in the most economical manner. This becomes almost certain by the following statement, which I have received from the most authentic possible source. It refers to an old-established German works and to the year 1889. (The "Mark" may be taken as slightly less than a shilling.

*Cost of 1000 kg. (= a ton) of real H<sub>2</sub>SO<sub>4</sub> in the shape of acid of 142° Tw.*

	Marks.
702 kg. pyrites 47 per cent. at 1½ M. per 100 kg. . . . .	10.53
13.1 kg. nitrate of soda at 20 M. . . . .	2.62
132 kg. coals at 1 M. . . . .	1.32
Wages for process . . . . .	3.36
Repairs of buildings and apparatus . . . . .	1.81
General expenses and management . . . . .	2.56
	22.20

This does not comprise amortisation of the plant, for which about 3 M. per ton must be charged, making the total = 25.20 M., or rather less than 25s. per ton of H<sub>2</sub>SO<sub>4</sub>, exclusive of packages.

For Germany, Niedenführ and Lütty in 1902 (*Z. angew. Chem.*,



1902, p. 242) give the following figures, referring to a plant-producing acid equal to 20 tons real  $\text{H}_2\text{SO}_4$  in twenty-four hours. When working with 50 per cent. Portuguese pyrites, 94.5 per cent. of the sulphur is utilised,  $3\frac{1}{2}$  per cent. being left in the cinders and 2 per cent. being lost in the chamber-process. Reckoning 2 M. per 100 kg. of pyrites (after deducting the value of the cinders), the cost of sulphur for 100 kg.  $\text{H}_2\text{SO}_4$  in the shape of chamber-acid is = 1.28 M. The consumption of nitric acid 36° Bé. with proper work is 1.1 part to 100  $\text{H}_2\text{SO}_4$ , or at a price of 19 M. per 100 kg. = 0.21 M.; coals, 12 parts at 16 M. = 0.19 M. per 100  $\text{H}_2\text{SO}_4$ . The labour is: 2 men for the steam-boilers, 3 men for moving the raw materials and cinders, etc., 8 men for pyrites-burners, 2 men for the chambers (the acid being automatically pumped); altogether 15 men at 3 M. = 45 M. or 0.225 M. per 100 kg. [Both the number of men and the wages are reckoned rather low.]

When employing mechanical dust-burners (pp. 474 *et seq.*) the wages for 100 kg.  $\text{H}_2\text{SO}_4$  decrease to 0.165 M., repairs 0.14 M. General expenses are not enumerated, as the calculation in question is to serve for a comparison of a cost of acid made by the chamber-process and such made by the contact-process; but this refers only to management, rates, taxes, insurance, etc., while the figure for amortisation and interest is of paramount importance in that respect.

*Depreciation*, in the case of sulphuric-acid works on the ordinary chamber-system, as erected in Germany during the last twenty or thirty years, may be reckoned on the basis of the following cost of plant for works turning out 20 tons  $\text{H}_2\text{SO}_4$  per day<sup>1</sup>:—

	Marks.
Ground-space 2500 sq. met. at 20 M.	50,000
Buildings	100,000
Steam-boilers and engines.	16,000
Pyrites-kilns and gas-flues.	48,000
Glover-chambers and Gay-Lussac	156,000
	<hr/> 370,000

<sup>1</sup> This estimate differs from that which Mr Niedenführ has made of the plant shown in Figs. 476 to 479 (p. 1232) in several respects. The last-mentioned estimate applies to a cheaper kind of chamber-building, to lump-burners in lieu of small-furnaces, and to a larger chamber-space than Mr Niedenführ thought necessary in his latest estimate.

Assuming  $7\frac{1}{2}$  per cent. average amortisation on plant, and 5 per cent. interest on total cost, that means 42,000 M. per annum, or per 100 kg.  $\text{H}_2\text{SO}_4$ , 0.583 M. for amortisation and interest. Where the plant is not constructed on rational and economical principles, this figure will be certainly exceeded, and in reality in many practical cases reaches 0.75 M. and upwards.

This shows the very great importance of saving in the first cost of plant, not in the wrong direction, but by increasing the yield of a certain cube of chamber-space by means of larger and better packed Glover and Gay-Lussac towers, by properly constructing the gas-flues, and, where necessary, applying mechanical means with a view to good draught, and principally by replacing part of the chambers by more energetically acting apparatus (pp. 647 *et seq.*), which promote better contact and better cooling of the gases, vapours, and misty particles. The principles for applying such "reaction-towers" are explained, pp. 656 *et seq.*

We have also shown on pp. 1233 *et seq.* how Nidenführ plans a rational chamber-system on that principle. The cost of such a combination of chambers and towers would be (for 20 tons  $\text{H}_2\text{SO}_4$  per diem):—

	Marks.
Ground-space 1850 sq. met. at 20 M.	37,000
Buildings	34,000
Steam-boilers and engines	16,000
Mechanical pyrites-burners and flues	50,000
Chambers and towers	98,000
	<hr/> 235,000

Reckoning  $7\frac{1}{2}$  per cent. amortisation on plant and 5 per cent. interest for plant and ground-space, we arrive at a sum of 26,600 M. = 0.37 M. per 100 kg.  $\text{H}_2\text{SO}_4$ .

With a [hypothetical] system consisting of towers only, as sketched p. 673, Nidenführ reckons the total cost of plant and ground-space at 84,000 M., for a production of 7200 kg.  $\text{H}_2\text{SO}_4$ . This is = 0.384 M. amortisation and interest per 100 kg.  $\text{H}_2\text{SO}_4$ , and shows that this part of the costs is practically no higher than the last calculated figure even for such a small factory (producing 7 tons  $\text{H}_2\text{SO}_4$  per day) when working entirely without chambers. [This part of the calculation is not, like the remainder, based on actual experience.]

Niedenführ now gives the following synopsis (founded on actual observations and at the date above mentioned) of the cost of 100 kg.  $\text{H}_2\text{SO}_4$  in the shape of chamber-acid or Glover-tower acid, without the cost of management, etc. :—

	Older system, Chambers only, hand-worked burners.	Combination of Chambers and Lungetowers, mechanical pyrites-burners.
	Marks.	Marks.
Pyrites . . . . .	1.28	1.28
Nitric acid . . . . .	0.21	0.21
Coals . . . . .	0.19	0.19
Wages . . . . .	0.225	0.165
Repairs . . . . .	0.14	0.12
Amortisation and interest .	0.583 to 0.70	0.37
	2.628 to 2.745	2.335

With the figures thus found Nidenführ and Lütj compare those referring to the *contact-process*. They reckon the cost of a contact-plant for 20 tons  $\text{H}_2\text{SO}_4$  per diem = 400,000 M., of which 37,000 M. are for ground-space. At 5 per cent. capital interest and  $7\frac{1}{2}$  per cent. amortisation on plant this is = 0.67 M. per 100 kg.  $\text{H}_2\text{SO}_4$ . The royalties vary from 75,000 to 150,000 M. = 0.104 to 0.209 M. per 100 kg.  $\text{H}_2\text{SO}_4$ . The cost of pyrites = 1.28 M. as before. Coals, according to various reports, are assumed to average 22 parts per 100  $\text{H}_2\text{SO}_4$ , or at 16 M. per ton = 0.352 M. per 100 kg. The wages must be rather higher, say 0.195 M. to 0.255 M.; repairs no less than in the case of chambers. Thus the authors arrive at a cost of from 2.529 to 2.996 M. per 100 kg.  $\text{H}_2\text{SO}_4$  made by the contact-process, which is essentially higher than the figures found previously for acid made by the old process. [It must be noticed that the latter estimates, but not the former, are based upon Nidenführ and Lütj's own experience.]

The above refers to acid up to the strength of Glover-tower acid. The case is very different when *stronger acids* are required; in the case of the contact-process the cost is exactly the same per 100  $\text{H}_2\text{SO}_4$ , but in that of the old process the cost of concentration must be taken into consideration.

For producing 20 tons  $\text{H}_2\text{SO}_4$  in the shape of 93 per cent. acid, the cost of a platinum concentrating-plant, inclusive of buildings and lead pans, varies between 140,000 and 260,000 M.

Apart from the loss of platinum (which in the case of Heraeus's platinum-gold apparatus, p. 1153, is from 0.23 to 0.30 M. per 20 tons), we must reckon 5 per cent. interest, and with cheaper (but more hard-worked) apparatus 3 per cent., with dearer apparatus 1½ per cent. amortisation, which together amount to a minimum of 29.20 and a maximum of 47 M. per 20 tons. From this, and taking as a basis the above-calculated cost of 2.335 M. per 100 kg.  $\text{H}_2\text{SO}_4$  in the shape of chamber-acid [cf. p. 1252, taking the more favourable figure, as brought out by utilising all rational improvements!] Niedenführ and Lütj make the following calculations:—

	Maximum cost. Marks.	Minimum cost. Marks.
20,000 kg. $\text{H}_2\text{SO}_4$ at 2.335 M.	467	467
3600 kg. coals at 16 M. per ton	...	57.60
or 4400 " " "	70.40	...
4 men at 3 M.	12	12
Loss of platinum (in case of Heraeus metal)	0.30	0.23
Repairs	10	7.50
Interest and amortisation	47	29.20
21,440 kg. acid of 93 per cent.	606.70	573.53
100 " " "	2.83	to 2.67

This shows that with large-sized platinum apparatus the expense is decidedly greater, although they suffer less than smaller apparatus.

Cast-iron concentrating-apparatus requires much more fuel (up to 50 per cent.), more labour, more repairs, and much more amortisation (10 per cent.), so that the total cost of acid is always much higher than with platinum apparatus. But it is quite different with Kessler furnaces (p. 1195), especially when combined with lead pans heated by the flues of pyrites-burners (p. 1093). This plant costs only 35,000 M. per 20 tons  $\text{H}_2\text{SO}_4$ , inclusive of buildings, and from this Niedenführ and Lütj derive the following calculation:—

	Marks.
20,000 kg. $\text{H}_2\text{SO}_4$ as chamber-acid at 2.335 M.	467
2000 kg. coke at 16 M.	32
1200 kg. coal at 16 M.	19.20
4 men at 3 M.	12
Repairs (from practical figures)	6
Amortisation and interest 15 per cent. on 35,000 M.	14.60
21,441 kg. 93 per cent. acid.	550.80
100 " " "	2.57

Up to 96 per cent. acid Kessler apparatus can be used as well. For acid up to 98 per cent. Heraeus stills should be used, and the costs would be:—

	Marks.
20,000 kg. $H_2SO_4$ as chamber-acid . . . . .	467
5800 kg. coal at 16 M. . . . .	92.80
6 men at 3 M. . . . .	18
Loss of platinum . . . . .	0.45
Repairs . . . . .	20
8 per cent. interest and amortisation on 380,000 M. . . . .	62.22
2050 kg. 97 to 98 per cent. acid . . . . .	660.47
100       "       "       " . . . . .	3.22

The same acid made by the contact-process would cost for 93 per cent., 2.35 to 2.79 M., for 97 to 98 per cent., 2.47 to 2.93 M. (in each case exclusive of management, etc.).

The following table gives a synopsis of the above calculation of costs (in Marks) of 100 kg. concentrated acid:—

(a) 93 per cent. $H_2SO_4$ .		Made in a Kessler furnace.	Made by the contact-process.	
Made in a platinum- gold still.			minimum.	maximum.
minimum.	maximum.			
2.67	2.83	2.57	2.35	2.79
(b) 97 to 98 per cent. $H_2SO_4$ .				
Made in a platinum- gold still.			Made by the contact-process.	
			minimum.	maximum.
3.21			2.56	2.93

From this Niedenführ and Lütj draw the following conclusions:—

For the manufacture of acid of 50° to 60° B $\acute{e}$ . (i.e. up to 78 per cent.  $H_2SO_4$ ) a rationally constructed system on the old process is more advantageous than the contact-process.

For acid of 93 per cent. the contact-process is more favourable than the old system with concentration in platinum, but it balances the old system with Kessler furnaces.

For acids of higher strengths the contact-process has a decided advantage over the platinum concentration, whether combined with cast-iron apparatus or not.

Lastly, Niedenführ and Lütj make the following remarks:—As chamber-acid, made by plant erected on modern principles, is decidedly cheaper than acid of 50° B $\acute{e}$ . made from anhydride, and the advantage of the contact-process comes in only with

stronger acids, *that strong acid must be cheapest which is made by dissolving  $\text{SO}_3$  made by the contact-process in chamber-acid or in acid concentrated to  $60^\circ \text{Bé.}$  by means of lead pans placed on the pyrites-burners.* For this they give the following calculations:—

	Minimum. Marks.	Maximum. Marks.
100 kg. 93 per cent. acid requires—		
33.6 kg. $\text{SO}_3 = 41 \text{ H}_2\text{SO}_4$ at 2.529 . . .	1.037	...
33.6 " " " at 2.996 . . .	...	1.224
66.4 kg. acid $60^\circ \text{Bé.} = 51.8 \text{ H}_2\text{SO}_4$ made by the chamber-process at 2.335 . . .	1.209	1.109
100 kg. acid 93 per cent. costs from . . .	1.146 to	2.433

This means that manufacturers, under present circumstances, ought to keep up their chamber sets, with the necessary improvements (towers, etc.), and make only so much  $\text{SO}_3$  by contact-processes as is required to bring up the chamber acid to the necessary strength. This, of course, in the first instance presupposes the employment of all rational improvements in the shape of first-class Glover and Gay-Lussac towers, plate-towers for part of the process, fan-blasts where necessary, etc.; and, secondly, it is only applicable for a somewhat large output. For smaller plants the combination of the chamber- and contact-process will not pay, and here the Kessler furnace comes in very well; or else several small makers might combine to start a common anhydride plant.

Hasenclever, in *J. Soc. Chem. Ind.*, 1911, p. 1292, makes the following statements concerning the costs of chamber plant and sulphuric acid at the present time in the best-conducted German works.

*Cost of Plant* (2 units of 5000 cb.m. = 176,500 cub. ft. chamber space, for an annual production of 20,000 tons sulphuric acid  $60^\circ \text{Bé.}$ , corresponding to  $5\frac{1}{2}$  kg. acid  $60^\circ \text{Bé.}$  per cubic metre in twenty-four hours or 11 cub. ft. per lb. sulphur in twenty-four hours).

	Marks.
Buildings and plant for crushing, conveying, roasting, and storing pyrites . . . . .	344,000
Buildings, chambers, boilers, engines, and concentrators (736 tons of lead at 300 M. per ton) . . . . .	624,000
Accessory plant (nitric acid, water supply, railway sidings, electric light, bath and meal rooms for workmen, works' railway, drains, etc.) . . . . .	89,000
	1,057,000
	4 L

Depreciation, 8 per cent., roundly 85,000 M.

The value of land is not taken into account.

*Manufacturing costs* of 100 kg. sulphuric acid 60° Bé.  
(= 142° Tw.).

				Marks.	
Roasting of pyrites—					
Available sulphur in pyrites	.	.	.	1.00	
Brushing and roasting	.	.	.	0.25	
Depreciation	.	.	.	0.14	Marks.
				<hr/>	1.39
Manufacture of sulphuric acid—					
Working of chambers (including repairs)	.	.	.	0.46	
Concentration	.	.	.	0.15	
Depreciation (chambers 0.25 M.; accessory plant 0.05 M.)	.	.	.	0.30	
				<hr/>	0.91
					<hr/>
Average cost of carriage in Rhineland				0.30	
Tank-wagons				0.10	
				<hr/>	
Cost (delivered free at consumers' works)				2.70	
4 per cent. interest on capital invested				0.20	
				<hr/>	2.90

The item of cost of available sulphur in pyrites will probably have to be modified (1) if the works can burn pyrites from their own mines; (2) if pyrites containing copper is treated and the yield of copper credited to the sulphuric acid account; (3) if sulphide of iron from gas works can be had at a low price; (4) if burner gases from zinc works can be bought on favourable terms.

According to Hasenclever, it is a mistake to believe that it is cheaper to make sulphuric acid from zinc blende than from pyrites, on the assumption that the sulphur contained in the blende has not to be paid for. At this day the charges for wages and fuel in roasting blende by hand amount to at least 1.50 M. per 100 kg. of sulphuric acid 60° Bé.; the loss of zinc and inefficient roasting may materially increase the costs. The charges for crushing, roasting, and depreciation are higher for blende than for pyrites.

For *America* the following calculations of the cost-price of

pyrites-acid is given in the United States *Mineral Resources* for 1886, p. 671 :—

2½ short tons of pyrites (46 per cent.) at 10 cents per unit per ton .	\$11.50
60 lb. nitrate of soda at 2½ cents . . . . .	1.50
5 cwt. of coal at \$4 per ton . . . . .	1.00
Wages . . . . .	3.00
Superintendence and management . . . . .	2.00
General jobbing repairs . . . . .	0.60
Interest on capital of \$100,000 at 10 per cent. . . . .	6.15
	<hr/>
	\$25.75
Produce 4½ tons of 50° Bè., cost per ton . . . . .	5.50

Stahl (*Z. angew. Chem.*, 1893, p. 54) quotes the cost of producing chamber-acid of 50° Bè. in the east of the United States as follows (in bulk):—

*A. From Brimstone.*

2.5 tons brimstone (5600 lb.) at \$21 . . . . .	\$52.50
225 lb. nitrate of soda . . . . .	4.50
200 lb. sulphuric acid 60° Bè. at \$0.40 . . . . .	0.88
4 men (including firemen) . . . . .	6.00
Wear and tear of burners, chambers, buildings . . . . .	5.40
Repairs . . . . .	2.70
Coals, lighting, etc. . . . .	2.00
Management . . . . .	5.00
Capital interest . . . . .	5.00
	<hr/>
13.5 tons chamber-acid cost . . . . .	\$83.98
1 ton     "     " . . . . .	6.22

*B. From Pyrites.*

5.5 tons pyrites (37 per cent. avail. sulphur) at \$6 . . . . .	\$33.00
180 lb. nitrate of soda . . . . .	3.60
250 lb. sulphuric acid 60° Bè. . . . .	1.00
Breaking pyrites and removing cinders . . . . .	1.40
6 men (including firemen) . . . . .	9.00
Wear and tear of burners, buildings, chambers . . . . .	5.50
Repairs . . . . .	2.75
Coals, lighting, etc. . . . .	2.00
Management . . . . .	5.00
Capital interest . . . . .	5.50
	<hr/>
11 tons chamber-acid cost . . . . .	\$68.75
1 ton     "     " . . . . .	6.25

The purification from arsenic, if there is very little present, costs 10 cents per ton.



Hence the costs are about the same, if a ton of pyrites with 37 per cent. available sulphur costs \$6.00, that is \$16.20 for the sulphur contained therein, against \$21 for Sicilian sulphur. The difference of \$4.80 represents the lower value of available pyrites sulphur in comparison with Sicilian brimstone. In the case of Spanish or other pyrites rich in arsenic, the difference in value must be taken = \$1.50 more, or = \$6.30. If, for instance, such pyrites with 47 per cent. sulphur costs \$8, the sulphur therein costs \$17.00 per ton, and this is the equivalent of a price of \$23.30 for Sicilian sulphur.

From comparative tables which William Wilke, M.E., and Dr H. P. Weidig, of Newark, have drawn up for the cost of producing sulphuric acid from pyrites or sulphur, I quote, with their permission, the following figures, choosing a medium-sized plant for producing 10,000 tons of sulphuric acid per annum (evidently chamber-acid of about 50° B $\acute{e}$ . is meant):—

	Pyrites.		Sulphur.	
1 Glover tower . . . . .	12 × 12 × 25 ft.		1 : 12 × 12 × 25 ft.	
2 Gay Lussacs . . . . .	6 × 35 ft.		2 : 6 × 35 ft.	
32 furnaces . . . . .	5 ft. kilns		1 : 16 × 20 ft. furnace	
Cost of whole plant (frame build- ings)	\$58,000		\$50,000	
Cost of whole plant (brick build- ings)	\$73,000		\$62,000	
Pyrites 49 per cent. available sulphur at \$7 (long ton) . . .	3776.68 tons	\$26,436	2075 tons	\$35,275
Sulphur at \$17 per 2000 lbs. . .	...		...	1,660
Nitre at 2 c. per lb. . . . .	...	1,660	...	1,800
Coal for air and steam . . . .	...	2,400	...	38,735
Total cost of material . . . .	...	30,496	...	1,500
Labour (1 manager) . . . . .	...	1,500	...	(2) 1,400
" (chambermen) . . . . .	...	(2) 1,400	...	(2) 1,100
" (furnacemen) . . . . .	...	(4) 2,200	...	(1) 400
" (labourers) . . . . .	...	(4) 1,600	...	...
Total cost of labour . . . . .	...	6,700	...	4,400
Repairs . . . . .	...	1,000	...	700
Interest (6 per cent. on plant and working expenses) . . . . .	...	6,180	...	6,000
Insurance, taxes, water, and office expenses . . . . .	...	6,342	...	6,200
Depreciation of plant . . . . .	...	(2%) 1,300	...	(1½%) 1,120
Total cost of yearly output . .	...	50,718	...	56,035
" per ton acid . . . . .	...	5.07	...	5.60



## CHAPTER XI

### THE MANUFACTURE OF NORDHAUSEN OR FUMING OIL OF VITRIOL, AND OF SULPHURIC ANHYDRIDE

ON pp. 280 *et seq.* the fuming or "Nordhausen" oil of vitriol has been described, and has been characterised as a mixture of

$$\begin{array}{c} \text{SO}_2\text{—OH} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{SO}_2\text{—OH} \end{array}$$
 sulphuric hydrate and pyrosulphuric acid, a compound

which has lately come into the market as "solid oil of vitriol."

Although in all probability fuming oil of vitriol is precisely that kind of sulphuric acid which was obtained first of all, and although about 1850 it was still manufactured in several places, and especially near Nordhausen, in Prussian Saxony, later on its manufacture, according to the only method formerly employed, was carried on exclusively in Bohemia, by the firm of Johann David Starck. The reason of this was that in this manufacture manual labour constitutes a very large portion of the expense, and that it requires a very large space and a great number of small apparatus, so that it can only pay under certain conditions rarely present. Owing to this, all other factories ceased to work, even those in the Harz (which, by the way, were not located at Nordhausen itself, where there was only a warehouse for the acid, but at Braunlage and Goslar).

So long as fuming oil of vitriol was only used for dissolving indigo (for which purpose it is very little employed now), the monopoly of the Bohemian firm was not very much felt; but since very large quantities of fuming acid were required in the mineral-oil industry, especially in the manufacture of alizarine and many other coal-tar colours, many efforts have been made

to produce that acid in another way; and success has at last been attained. The attempt was made in two ways:—first, by trying whether the ferric sulphate obtained by the Bohemian method cannot be replaced by other sulphates yielding their acid on heating, partly or entirely, as anhydride; and, secondly, trying whether the anhydride, or its solution in sulphuric hydrate cannot be obtained synthetically.

We shall, in the first place, describe the method by which the oil of vitriol was formerly exclusively obtained—namely, from “vitriol-stone”—which rests on the fact that ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , at a red heat splits up into ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and sulphuric anhydride ( $3\text{SO}_3$ ), the latter of which is partly decomposed into  $\text{SO}_2$  and  $\text{O}$ .

*The Manufacture of Fuming Oil of Vitriol in Bohemia.*

All former descriptions of this manufacture have been rendered obsolete by that given by E. V. Jahn in Wagner's *Jahresber.*, 1873, p. 220. We shall give an abstract of the latter, adding some supplementary notes.<sup>1</sup>

The basis of the whole manufacture consists of certain slates, which contain from 1 to 31 per cent. of pyrites and are distinguished from ordinary roofing-slates by their darker colour and high specific gravity; analyses of these “vitriol-slates” are given in our second edition, p. 836. The oxidability of these slates has led to a special industry, which has existed since the sixteenth century. When rich in alumina (which is only exceptional), the slates serve for making alum; when poor in alumina and rich in pyrites, for copperas and “vitriol-stone” (*Vitriolstein*), *i.e.* ferric sulphate—from which naturally followed the manufacture of fuming oil of vitriol (“oleum vitrioli”). The Pilsen sulphur-works are already mentioned in 1526. The fuming oil of vitriol is the oldest form of sulphuric acid, and was first manufactured in Bohemia. The Thirty Years' War destroyed that industry, which was transferred to the Nordhausen country, and returned to Bohemia only in 1778 on a

<sup>1</sup> The present account is much shorter than that given in our second edition, pp. 835 *et seq.*, the above industry having been discontinued in 1894, but it still possesses sufficient interest to be described here in an abridged form.

small scale, since 1792 on a larger scale, when Johann David Starck took it in hand, at first with the assistance of men obtained from the Nordhausen factories.

The manufacture is carried on as follows:—The schist is broken up by stone-breaking machines, and tipped into large terrace-shaped heaps, leaving both horizontal and perpendicular air-channels. By means of a system of spouts water can be sprinkled all over the heaps. The process of oxidation by weathering lasts about three years; and very large heaps having been made at first, strong lyes are always obtained. The ores, on lying in the moist air, become hot; the pyrites is oxidised, first to ferrous sulphate, then to ferric sulphate, along with a little aluminium sulphate. These salts, together with the pre-existing soluble salts, are lixiviated by water conveyed in the above-mentioned spouts. The brown liquors, possessing a density of generally  $28^{\circ}$ , and up to  $38^{\circ}$  Tw., are run into wooden reservoirs, where they remain some time for settling and are a little concentrated by spontaneous evaporation and also more highly oxidised. Then they are concentrated by top-heat in brick-furnaces, up to  $77^{\circ}$  Tw.; the soot and ashes are allowed to deposit in settling-tanks; and the clear liquor is further evaporated in cast-iron boilers to a syrupy consistence. If then run on to the floor, it solidifies to "*crude vitriol-stone*." This is a hard, pale green or yellowish-green mass, containing still a good deal of ferrous sulphate and water of crystallisation. In order to remove the latter and to oxidise the former, it is calcined in open roasters. The *calcined vitriol-stone* is essentially anhydrous ferric sulphate; it is yellowish white, dissolves in water with a reddish-yellow colour without leaving any large residue; and the solution has a strongly acid reaction. It still contains a little ferrous sulphate and constantly, in variable quantities, aluminium sulphate along with a little magnesium and calcium sulphates. It takes from 6 to 20 tons of schist to make one ton of vitriol-stone. The stone formerly yielded only about 33 per cent. of "*oleum*"; later on, however, owing to improved processes, the yield was from 40 to 50 per cent.

The vitriol-stone is distilled in four works, containing 120 "*oleum-furnaces*." These are the well-known *galley-furnaces*, shown in our second edition, p. 840. The calcined

vitriol-stone is broken by crushing-rollers and charged into retorts made of fire-clay. On each side of the galley-furnace there are four tiers of 34 retorts each, the bottoms of those in the centre nearly touching each other. A fifth tier is formed at the top by 34 large retorts, open on both sides, reaching right across the furnace, and each side is provided with a receiver. Each of the smaller retorts also is connected with a receiver, large enough for holding the product of four or five distillations. The necks of the receivers are narrower than those of the retorts; they are put into the latter, and the joint plastered with clay. Such a furnace thus contains 272 small and 34 large oleum-retorts and 340 receivers. The lower part of the furnace, where the fireplace, grate, and ash-pit are located, is made of solid masonry; the upper part consists of a light arch, perforated for each retort in such a way that the necks of the retorts are held without any further support. The bottom tier of the receivers rests upon the brickwork, the higher tiers on wooden laths.

Into every retort is ladled, on the average, 750 g. of vitriol-stone. The yearly consumption at Starck's works was 724,000 retorts and 40,000 receivers (previously twice as much). They are made at private potteries near the works, and thus cost only about 1d. to 1½d. apiece.

At the beginning of the distillation the temperature is slowly raised, so that after four hours the bottom tier of retorts has only attained a red-heat. During this time the retorts are left open; and consequently nearly all the ferrous sulphate still present is oxidised to ferric sulphate. With a higher heat aqueous vapour and sulphurous acid appear at the mouths of the retorts, generated from aluminium sulphate and still existing ferrous sulphate. Then thick vapours of sulphuric anhydride follow, which indicate the time for putting on the receivers. As the ferric sulphate simply splits up into  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$ , some liquid containing water must be put into the receivers, in order to condense and dissolve the sulphuric anhydride. This may be either rain-water or ordinary oil of vitriol. In the former case, ½ lb. of water should be put into each receiver, and it takes four or five distillations from the retort to attain the usual concentration of the oleum (79° Bé.). If the receivers have been charged with sulphuric acid of

66° Bé. (= 168° Tw.), it takes only 3 or 4 distillations to get it up to 80° Bé.

When the oleum has reached sufficient concentration, which the workmen recognise from the speed with which a wood splinter, dipped into it, is charred, it is filled into stoneware bottles and left for a week to settle, after which time the clear acid is drawn off from the deposited mechanical impurities.

The ferric oxide remaining in the retorts (about 33½ per cent.) is known by the name of *caput mortuum, colcothar, English red*, etc. (In England a similar article is called "Venetian red.") It is raked out of the retorts after each distillation, and exhibits different colours according to the degree of heat to which it has been subjected. The lower tiers yield it of darker, the upper ones of lighter colour. In the crude state it was very difficult to sell as a common pigment or polishing-powder. J. D. Starck improved this article very much by proper treatment; so that in 1872 1000 tons of it were sold, of nineteen shades and forty-one grades, especially for painting ships. It is ground under French mill-stones and again calcined with addition of common salt and at a certain temperature. The yellow shades are obtained by an addition of 2 per cent. of salt, igniting for an hour, and gradual cooling in a closed space; the brown shades, by adding 4 per cent. of salt; the purple shades, by 6 per cent. of salt, igniting for six hours at a gradually increasing heat, and rapid cooling. The igniting takes place in fireclay pipes lying in galley-furnaces similar to the oleum-furnaces, each of them containing sixty pipes. Unless the temperature is exactly regulated, the product becomes dark brown, and is then of little value. The best is contained in the two top tiers. After the igniting and cooling, it is sifted and levigated; by mixing the three above-named principal shades, the commercial shades between yellow, purplish red, and dark purple are obtained, which now only require drying and packing.

The small size of the retorts used for decomposing the vitriol-stone, and the large number of these apparatus consequently necessary, are evidently to be explained by the fact that in larger apparatus the heat would penetrate too unequally and would cause great loss by overheating one part and insufficiently heating another part of the charge.

## 1264 MANUFACTURE OF FUMING OIL OF VITRIOL

From Stolba (*Fischer's Jahresber.*, 1885, p. 316) we will only quote the following analyses:—

### 1. *Vitriol-stone.*

Ferric sulphate	50.17
Aluminium sulphate	11.94
Ferrous	1.35
Magnesium	1.17
Calcium	0.33
Copper	0.20
Sodium	0.11
Potassium	0.13
Sulphuric acid	1.49
Silicic acid	9.10
Traces of Mn, As, P <sub>2</sub> O <sub>5</sub>	...
Water	23.31
	99.30

### 2. *Caput mortuum.*

Ferric oxide	74.62
Alumina	12.53
Magnesia	3.23
Lime	0.82
Sulphur trioxide	5.17
Silicic acid	1.17
Copper oxide	0.20
Water	1.30
	99.04

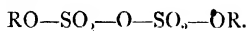
From a private source we can add that under the most favourable circumstances the yield from 100 parts of ferric sulphate, with 52 to 54 per cent. SO<sub>3</sub>, is hardly 36 parts of sulphuric anhydride testing 95 to 96 per cent., which is, of course, dissolved in the acid contained in the receivers.

In 1792, 1 cwt. fuming oil of vitriol cost in Bohemia 50 fl. (say £5), in 1873, 10 fl. (£1); the production in 1832 was about 1000 tons, in 1846, 3000 tons, in 1873, 3360 tons, in 1884, 4350 tons. At Bras the last galley-furnace was stopped in 1894. In 1900 the Bohemian manufacture from vitriol-stone was definitely abandoned.

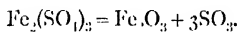
### *The Production of Sulphuric Anhydride and Fuming Oil of Vitriol from artificially prepared Sulphates.*

Two ways are possible for preparing SO<sub>3</sub> from sulphates, viz. either employing such sulphates which split up at a

sufficiently low temperature, or employing those compounds which stand midway between  $\text{SO}_3$  and the sulphates—that is, pyrosulphates of the type



The only representative of the former class is the *normal ferric sulphate*,  $\text{Fe}_2(\text{SO}_4)_3$ . Many other sulphates can be decomposed by heat, as those of aluminium, zinc, copper, etc.; but in all cases, except the first, the decomposition takes place only at temperatures at which  $\text{SO}_3$  itself splits up into  $\text{SO}_2$  and O. Thus, for instance, the zinc sulphate, so easily formed in roasting blende, on heating to a bright red-heat yields  $\text{ZnO}$ ,  $\text{SO}_2$ , and O, but no  $\text{SO}_3$ . But ferric sulphate is already decomposed at a dark red-heat, scarcely visible in daylight, so that the  $\text{SO}_3$  given off is not yet decomposed, and the reaction is simply:



This reaction can never be realised to its full extent, as it is impossible to bring all the contents of the decomposing-apparatus exactly to the minimum temperature required; a considerable portion of the mass is too much heated, and, moreover, much of the  $\text{SO}_3$  first formed is subsequently overheated in contact with hotter parts of the mixture or the walls of the apparatus, so that part of the  $\text{SO}_3$  is always split up into  $\text{SO}_2$  and O, and is thus lost, unless these gases are recombined by special means, viz., by the contact-process (*cf.* below).

Both this circumstance and the difficulty of preparing ferric sulphate cheaply enough have militated against the, apparently so easy, imitation of the Bohemian process, which consists in treating ferric oxide with strong sulphuric acid, heating the mixture till all the water has been driven off and dry ferric sulphate has been produced, and continuing the heating at a higher temperature, with condensation of the sulphuric anhydride evolved, the residue of ferric oxide serving over and over again for the same purpose.

This process is much more difficult than it appears and has never been successfully carried out.

An invention intended to improve the Bohemian process, but applicable also to sulphates prepared in other ways, and



introducing already a "contact"-process, was made by R. Schubert (Ger. P. 52000, 4th April 1889). He states that the formation of sulphur dioxide is the principal cause of the loss which, in the best case, amounts to 30 per cent. of the total  $\text{SO}_3$ , and in the case of large vessels or furnaces may destroy all the  $\text{SO}_3$  present. This is caused by the prolonged contact of free  $\text{SO}_3$  with the red-hot sides of the retorts; and this circumstance had confined the Bohemian process to the use of small vessels, involving a large consumption of fuel and of clay retorts, together with the necessity of employing much skilled labour and other drawbacks, such as the escape of acid smoke into the atmosphere. All this is avoided by bringing about the decomposition of the sulphates in a partial vacuum, and removing the vapours by aspiration. This can be done with ferric sulphate obtained in the Bohemian manner from schist, or with artificially prepared sulphates of iron, etc. The operation is carried on in a horizontal shallow fireclay retort, provided with a cast-iron mouth-piece like that of gas-retorts. This mouth-piece contains an opening for charging and discharging, and a stirring-rake sliding in a stuffing-box; when not at work, the rake is pulled back towards the front so as to be out of the heated portion of the retort. Above the furnace is placed a cast-iron tube, containing a suitable filtering-substance for the gases, such as broken glass or pottery, asbestos, glass-wool, and the like. This gas-filter communicates on the one side with the retort, on the other side with a cast-iron air-pump. The vapours, drawn by this pump from the retort and passed through the filter, are forced through an upright cast-iron cylinder, lined with earthenware and containing a number of perforated dishes, charged with 10 per cent. platinised asbestos. The apparatus is heated by the waste gases from the retort-fire and serves for regenerating  $\text{SO}_3$  from the small quantities of  $\text{SO}_2$  and  $\text{O}$  formed in the retort. From here the vapours pass into cast-iron condensers, where they are absorbed by strong sulphuric acid, the condensation being aided by pressure. During the operation the sulphate within the retort is raked up several times; but while this is done, the pump is stopped in order to avoid any dust being drawn away. The employment of a vacuum causes a quick decomposition of the ferric sulphate, with but slight

formation of  $\text{SO}_2$ ; the duty performed by the apparatus is large, and the consumption of fuel much less than before. The residue is not overheated, as is the case in the lower ranges of the galley-furnace, and is thus better adapted for use as a paint; from the same reason it is also possible to use it over again for forming ferric sulphate. If sodium sulphate is to be used, the retort is made with a dished bottom, lined with platinum. This is charged with sodium sulphate once for all; by adding sulphuric acid of  $140^\circ$  Tw. bisulphate is formed, which (in the same way as is done in the case of ferric sulphate) is first heated without connection with the condensers till all the water has been driven out, and fumes of  $\text{SO}_3$  and  $\text{SO}_2$  appear, whereupon the connection is established and the heating continued. The residue in the retort is again treated with ordinary sulphuric acid, and thus used over and over again (*cf.* Ncale's patent *infrà*, p. 1296).

I am not aware whether Schuberth's process has been practically carried out, and if so, with what success.

It is, however, possible that the following process may be profitable, since under the special circumstances of the case the acid costs nothing (or less than nothing, considering the trouble caused by the necessity of removing it), and the value of fuel in the special local case is also extremely slight. Ragsine and Dworkowitsch (Ger. P. 43453) employ the *acid-tar* (*sludge-acid*) produced in the purification of crude petroleum in enormous quantities and containing up to 90 per cent. free acid (*cf. supra*, p. 1179). This they mix with ferric oxide. This mixture produces a strong reaction, so that part of the water evaporates; and sometimes it is even necessary to cool, as the decomposition of the sulphate begins at  $150^\circ$  C. The solid mass produced is crushed and dried, and is heated to  $300^\circ$  or  $500^\circ$  C. Fig. 486 shows the furnace employed for this purpose. It consists of a muffle A with a very low arch; through the tuyère *b* dry air is injected, and the heavy vapours of sulphuric anhydride are drawn off through *c*. The waste fire-gases serve for drying the mass in pan B.

Some have proposed to make fuming O.V. from *ferrous sulphate* (copperas), which, on calcination, yields basic ferric sulphate,  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ ; but this is evidently even much less promising than the process starting with  $\text{Fe}_2\text{O}_3$  and  $\text{H}_2\text{SO}_4$ .

and the calculations made by Schemfil (Fr. P.<sup>1</sup>, 2nd December 1869; *Monit. Scient.*, 1870, p. 492) are entirely worthless.

Anzies (Fr. P. 420675) mixes anhydrous calcium sulphate with ferric oxide and heats to  $800^{\circ}$  to  $1300^{\circ}$ . The escaping mixture of  $\text{SO}_2 + \text{O}$  is passed over the oxides of Mn, Wo, or Th at  $200^{\circ}$ , whereby  $\text{SO}_2$  and O combine to form  $\text{SO}_3$ .

*Magnesium sulphate* was patented for this manufacture by Sonstadt (3rd March 1875) in the shape of natural kieserite or calcined Epsom salts. The operation was to be carried

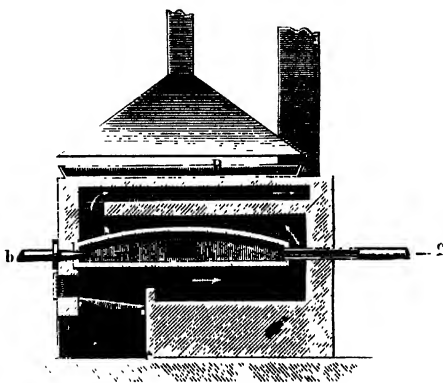


FIG. 486.

out exactly as with ferric sulphate. But it is a fact (cf. Wagner's *Jahresber.*, 1876, p. 327) that magnesium sulphate on calcination yields very little  $\text{SO}_3$ , mostly  $\text{SO}_2$  and O.

*Sodium pyrosulphate*,  $\text{Na}_2\text{S}_2\text{O}_7$ , is readily produced by heating the easily manufactured bisulphate,  $\text{NaHSO}_4$ , till the chemically combined water is expelled. On heating to a higher temperature the pyrosulphate itself gives off sulphuric anhydride,  $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$ , and the normal sodium sulphate left behind can be employed for again making bisulphate. This has formed the basis of more than one proposal. \*

Prelier (B. P. 29th June 1847) proposed to prepare fuming oil of vitriol by the following process, which is said to have been carried out in France on a large scale, evidently only for a short time (if at all). One hundred parts of calcined

sodium sulphate are mixed with 2 parts of potassium sulphate and 2 parts of gypsum, charged into retorts of sandstone (?), and a sufficient quantity of concentrated sulphuric acid added to form bisulphates. Then, heat is applied; first all the water distils over, then sulphuric acid of  $77^{\circ}$ , then of  $106^{\circ}$ , then of  $170^{\circ}$  Tw., and at last fuming acid. The latter is recognised by the drops falling into water producing a hissing noise; then a receiver filled with acid of  $170^{\circ}$  Tw. is put on. This acid sometimes contains sodium sulphate. The residue in the retort is always used for the same purpose.

Wallace obtained a B. P. (2285 of 1876) for heating sodium bisulphate in fireclay retorts; the formed anhydride or fuming vitriol is to be collected in earthenware jars with a lid perforated for receiving the gas-pipe, which can be replaced by a plain cover; thus the acid can be sent out in the receiver itself, and the fumes emitted in pouring it from one vessel into another are avoided. The fumes first coming over, which consist of aqueous sulphuric acid, are condensed separately. The sodium sulphate remains in the retort, and is always reconverted into bisulphate by adding sulphuric acid; so that a continuous operation is possible.

Dr Adolph Clemm (personal information) introduced the bisulphate process at the works of G. C. Zimmer at Mannheim in 1877, and already in May 1877 he delivered eighty stone jars of 40 per cent. fuming acid to the Badische Aniline and Soda works. This process was carried on for a number of years, until the adoption of the contact-process by the Badische and other factories made competition impossible.

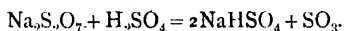
*Fuming Sulphuric Acid from the Action of Boric Acid upon Sodium Bisulphate* (Kerl-Stohmann, *Chem.*, 3rd. ed., vi. p. 156).—This method has probably never advanced beyond the state of a suggestion.

*From Magnesium Sulphate and Sodium Pyrosulphate mixed.*—Wolters obtained a Ger. P. (3110 of 1878) for this purpose.  $\text{MgSO}_4$  acts upon  $\text{Na}_2\text{S}_2\text{O}_7$  considerably below a red-heat, a double salt ( $\text{MgSO}_4, \text{Na}_2\text{SO}_4$ ) being formed and  $\text{SO}_3$  being liberated. Instead of  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , etc., may be employed. The remaining salt is reconverted into the mixture first employed by treatment with water and ordinary sulphuric acid, and exposing to sufficient heat. The value

of this process is said to consist in the fact that the anhydride is liberated at a much lower temperature than from sodium pyrosulphate alone, thus preventing much loss, causing a larger yield of  $\text{SO}_3$ , and permitting the use of ordinary fire-proof materials without any extraordinary wear and tear. (Experiments made in my laboratory with Wolters's process have to a great extent confirmed these statements.)

An additional Ger. P. (6091 of 1878) contains a simplification which I in my laboratory experiments had employed as a matter of course. Instead of treating the residue from distillation with water and separating the salts by crystallisation, the dry double salt ( $\text{Na}-\text{SO}_4-\text{Mg}-\text{SO}_4-\text{Na}$ ) is ground and treated directly with sulphuric acid (1 equivalent to 2 of salt, as otherwise half the acid passes over in the hydrated state).

On the large scale Wolters's magnesium process does not seem to have been successful. But this appears to have been the case with a further process of his, patented in 1881 (Ger. P. 12295). He prepares sodium pyrosulphate, in the usual manner, by heating the acid sulphate  $\text{NaHSO}_4$ , till the water has been expelled. When adding to the pyrosulphate a large quantity of monohydrated sulphuric acid there is a decomposition according to the formula :

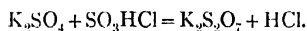


The  $\text{SO}_3$  is distilled off, and the hydrosodic sulphate is used for starting the process over again. This process has been actually at work in several factories, e.g. at Einergraben near Barmen during the years 1884 to 1889 (communication from Dr Adolph Arndt).

A further patent of Wolters's (Ger. P. 15639) shows that on heating a mixture of a pyrosulphate with concentrated sulphuric acid in cast-iron vessels a crust of iron sulphide is formed, which firmly adheres and resists the acid in the process of distillation so long as the hydrosodic sulphate remains in the retort.

A detailed study of the pyrosulphates has been made by H. Schulze (*Ber.*, xvii. p. 2705); we can give only a very short abstract here. Dry potassium or sodium sulphate absorbs  $\text{SO}_3$  at the ordinary temperature with considerable evolution

of heat; but if a complete potassium pyrosulphate is to be formed, a higher temperature is necessary (soaking with  $\text{SO}_3$  and distilling off the excess at  $100^\circ$  to  $120^\circ$ ). The sodium salt, treated in this manner, contains only 85 per cent.  $\text{Na}_2\text{S}_2\text{O}_7$ . Many other bases form pyrosulphates as well. The method of Berzelius for preparing pyrosulphates, by heating the hydrosulphates, gave unsatisfactory results; a better result is obtained by heating sulphates with chlorosulphonic acid (employing an excess of this, which is afterwards distilled off), the reaction being:



[Unfortunately chlorosulphonic acid has hitherto been prepared only by means of  $\text{SO}_3$ , so that that process is not available for technical purposes.]

An excellent process for preparing sodium pyrosulphate is that of Baum (Ger. P. 40696). Two hundred and forty kg. hydrosodic sulphate, or else 142 neutral sodium sulphate, and 98 kg. monohydrated sulphuric acid are put into a cast-iron retort, provided with agitating-gear and connected with an air-pump. The latter is set in motion to produce a vacuum, and the retort is heated first to  $260^\circ$ , afterwards, with constant agitation for five to eight hours, to  $300^\circ$  or  $320^\circ$ . Most of the water comes off between  $260^\circ$  and  $280^\circ$ , if the vacuum is equal to a column of 500 or 600 mm. mercury; the heating to  $320^\circ$  is only done to make quite sure of finishing the reaction. It is useful to place between the retort and the air-pump a cooler, connected by a glass tube with a receiver. When no more water is observed to run down the glass tube the reaction is finished, and the melted mass is poured out to solidify into plates consisting of pure  $\text{Na}_2\text{S}_2\text{O}_7$  (*cf.* Schuberth's process, p. 1266).

*Other Processes for the Manufacture of Sulphur Trioxide or Fuming Sulphuric Acid (apart from contact-processes).*

*Dehydration of Sulphuric Acid by Metaphosphoric Acid.*—Nobel and Fehrenbach (B. P. 10860 of 1884) pass the vapours of boiling strong sulphuric acid over lumps of metaphosphoric acid heated to  $320^\circ$ . This acid retains the water and part of the sulphuric acid, whilst vapours of sulphuric anhydride are

given off and are condensed in the usual manner. The operation is performed in a vessel of glass or platinum heated in a sand-bath, the sulphuric acid vapours being passed in by a tube reaching nearly to the bottom. The vapours of  $\text{SO}_3$  escape at the top, the liquefied mixture of phosphoric and sulphuric acid runs out at the bottom, and is reconverted into metaphosphoric acid by evaporation and calcination at a low red-heat. [Up to the present no material is known by which this process could be carried out. Glass or platinum certainly do *not* resist the action of fused phosphoric acid for any length of time.]

*Sulphuric Anhydride from Chamber-crystals.*—O. von Gruber (Ger. P. 27726) proposed making  $\text{SO}_3$  from nitrososulphuric acid (chamber-crystals) by heating them with dry air and sulphur dioxide at a higher temperature, and recovering the nitre gas evolved.

*The Utilisation of the Sulphuric Anhydride contained in Pyrites-kiln Gases.*—It is well known that ordinary pyrites-kiln gases contain a somewhat considerable quantity of sulphuric anhydride, which may occasionally amount to nearly 10 per cent. of the total sulphur acids present (*cf.* p. 565). This fact has been utilised by various inventors. Majert and Messel (B. P. 1201 of 1878) pass the burner-gas through concentrated sulphuric acid, which dissolves the  $\text{SO}_3$ , and can thus be brought up to real monohydrate,  $\text{H}_2\text{SO}_4$ , or even further; but undoubtedly this acid must be saturated with  $\text{SO}_2$  as well, and this will make it useless for most purposes.

I. J. Cox and The du Pont de Nemours Powder Company (Amer. P. 1002824) state that the preparation of fuming O.V. by passing gases containing anhydrous  $\text{SO}_3$  through a comparatively small quantity of concentrated sulphuric acid suffers under the drawback that the heat of the reaction and the quickly increasing concentration of the absorbent interfere with the absorbing process. They remedy this, firstly, by keeping both the gases and the absorbing acid at a certain optimum of temperature, viz., from 29.4 to 46° C.; and secondly, by regulating the proportion between the absorbing acid and the gases containing  $\text{SO}_3$  in such manner that it does not get below the rate of 43 : 1. The B. P. is 8528 of 1911, taken out by A. J. Boulton, as communication from Cox.

Blackmore (B. P. 27907 of 1904) oxidises  $\text{SO}_2$  by an oxidising compound in such manner that the heat produced is taken up by an endothermic reaction taking place in the same space, and thus the dissociation of the  $\text{SO}_3$  formed is prevented.

R. Frank (Ger. P. 194879) burns sulphur with oxygen under a pressure of at least 100 atm., which causes the quantitative formation of  $\text{SO}_3$ . The gas coming out of the compressor is allowed to expand and cool down, which causes the  $\text{SO}_3$  to crystallise out as a solid; the escaping oxygen is used over again and its rapid extension causes a further lowering of the temperature, preventing loss of  $\text{SO}_3$ . The yield is stated to be quantitative.

O. Bender (Ger. P. 195810) exposes a mixture of  $\text{SO}_2$  and O, with or without N, to the action of an oxyhydrogen flame, in a furnace similar to a gas-producer, fitted with a grate for fuel and above it a hopper for charging fuel, brimstone, or some sulphur-containing material.

Hilbert (Fr. P. 389032; Ger. P. 207761) produces  $\text{SO}_3$  in the manufacture of glass by employing calcium or barium sulphate, in lieu of the carbonates, in that manufacture. A mixture of gypsum, sand, and alkali-sulphate is completely decomposed in that manner, all the sulphur being evolved as  $\text{SO}_3$ ; a temperature of about  $1400^\circ$  is most suitable. Many waste sulphates may be thus utilised. In electric furnaces the work can be done at a temperature of  $1250^\circ$ ; the absence of  $\text{CO}_2$  from the gases very much facilitates the process. In *Chem. Zeit.*, 1910, p. 390, it is stated that this process has been successfully carried out on a manufacturing scale.

Olga Niedenfuhr (Ger. P. 230533) describes the continuous production of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  from fuming O.V. by quickly heating it to the temperature of distillation by means of pyrites-burner gases, directed immediately on the top of, or into the O.V., where the  $\text{SO}_3$  contained in them is also utilised. New O.V. is continuously fed into the still.

Mc. Fetridge (Amer. P. 988646) prepares sulphuric anhydride by injecting finely divided metallic sulphides, with a regulated volume of air, into a furnace where the S is converted into  $\text{SO}_2$  and the metals into oxides. These oxides, suspended in the gas, are supposed to free the gases from arsenic and to convert by catalytic action the  $\text{SO}_2$  into  $\text{SO}_3$ .



Briggs and Merriam, Assignors to the General Chemical Company (Amer. P. 1013638) bring sulphuric anhydride and air into contact with finely divided sulphuric acid (94 to 95.5 per cent.), which is made to move in an opposite direction to that of the mixture, the latter preferably passing upwards and meeting the acid in a descending film. The apparatus is cooled outside, so that all the  $\text{SO}_3$  is absorbed.

*Application of Electricity for manufacturing Sulphuric Anhydride.*—Léon (Fr. P. 206088 of 9th June 1890) proposed manufacturing sulphur trioxide by the electrolysis of sulphuric acid of  $66^\circ$  or  $65.5^\circ \text{Bé.}$  The current must not exceed  $\frac{1}{10}$  ampère per square centimetre, in order to avoid heating. Thus  $\text{SO}_3$ , H, and O are produced; the former is condensed and the latter escape. The electrodes are made of platinum or carbon; they are kept 2 or 3 mm. apart by means of asbestos or glass-wool, which reduces the electrical resistance of the bath to 2 or 3 ohms per centimetre, and permits a near approach to the theoretical yield, viz., 1 kg.  $\text{H}_2\text{SO}_4$  for each half horse-power per hour, or 1 kg. of 45 per cent. Nordhausen acid. Sometimes a deposit of sulphur is formed on the cathode, but this is got rid of by reversing the current.

Some more details respecting Léon's process are given in his Ger. P. 57118. He works in a cast-iron tank, cooled from without and covered with a slate slab. In the centre is the hollow platinum anode, with a water-cooled brass box inside. It is surrounded by an open, annular cathode, provided with open passages at the bottom, and supported by glass-coated copper rods, ending in platinum caps. With currents of very low density (0.1 ampère to 1 sq. cm.), in which case the voltage can be lowered to 2.5, the electrodes are 3 cm. high, and consist of crude copper, coated on both sides with platinum-foil soldered with gold; these are coiled in a spiral shape and kept at a proper distance by glass rods and asbestos cord. Per hour 1 kg. anhydride can be produced with an expenditure of 0.9 h.p., or 1 kg. fuming acid or  $68^\circ \text{Bé.}$  with an expenditure of 1.2 h.p.

Garraway (B. P. 1755 of 1903) passes sulphurous acid gases, together with air, ozonised by electrical discharges and oxides of nitrogen up a column or tower.

Riesenfeld (Ger. P. 229274) prepares  $\text{SO}_3$  by the action of electric discharges on burner gases, while keeping the tempera-

ture below  $46^{\circ}$ , in which case ozone is formed and the reaction  $3\text{SO}_2 + \text{O}_3 = 3\text{SO}_3$  takes place. The reaction is almost quantitative, but care must be taken to keep the temperature below  $46^{\circ}\text{C}$ .

*Application of the Ultraviolet Light-rays* for manufacturing sulphuric anhydride.—The manufacture of sulphuric anhydride by the combination of  $\text{SO}_2$  with  $\text{O}$  to  $\text{SO}_3$  under the influence of the ultraviolet rays of light was patented by Cœhn and Becker (Ger. P. 217722). According to them an essential condition is the keeping up of a small intensity of the light. The mercury lamps, used for this purpose, must not be of the type most appropriate for lighting purposes, but they must be worked with a small pressure of mercurial vapour. By diminishing the intensity of the light, its catalytic action is retarded; hence it is necessary to apply heat, up to  $300^{\circ}$ , for accelerating the process. In the place of pure  $\text{O}$  and  $\text{SO}_2$ , air and burner gases may be employed. The light reaction obeys the law of the action of masses; hence the yield is increased by increasing the concentration of oxygen.

Daniel Berthelot and Gaudechon (*Comptes rend.*, CL., p. 1517; *Chem. Centr.*, 1910, ii. p. 365) found that  $\text{SO}_2$  by the ultraviolet rays of light, even in the presence of oxygen, is split up into its elements; the split-off oxygen by a secondary reaction oxidises the  $\text{SO}_2$  still present to  $\text{SO}_3$ .

*The Manufacture of Sulphuric Anhydride (also of Fuming and Ordinary Sulphuric Acid) by "Contact"-Processes.*<sup>1</sup>

This manufacture, which, after a number of unsuccessful attempts, made during a period of many years, was definitely established in the last quarter of the nineteenth century, has during the last few years enormously increased in importance, and apart from supplying all the fuming sulphuric acid now

<sup>1</sup> The history of the contact-processes for the manufacture of sulphur trioxide, etc., has been treated by Winkler, in *Z. angew. Chem.*, 1905, pp. 1512 *et seq.* and 1654 *et seq.* His paper contains nothing essentially different from what had been already given in the former editions of this treatise. One of his statements, concerning the action of arsenic as "contact-poison," was rectified by the Badische Anilin und Sodafabrik, *loc. cit.*, p. 1902.

used, bids fair to oust the time-honoured lead-chamber process, at least for the manufacture of highly concentrated acid.

Up to 1899 very little was known as to what the various factories were doing in that respect, complete secrecy being observed thereon. The ice was broken by the publication of the patents taken out almost simultaneously by the Badische Anilin und Sodafabrik, by the Hoechst works (Meister, Lucius, & Brüning), and the Mannheimer Verein chemischer Fabriken. But even then most of the circumstances of the rise and the present state of this industry remained unknown. This veil was to a certain extent lifted by a lecture given by Dr Knietsch, of the Badische Anilin und Sodafabrik, before the German Chemical Society and published in the *Ber.*, 1901, vol. xxxiv. pp. 4069 *et seq.*

It is needless to say that I have fully drawn upon this source in my account, as well as upon everything else accessible in print; but I have had, moreover, the good fortune to receive, for the purpose of this work, extended and most valuable communications, embracing very many hitherto unpublished facts, from most of the firms or inventors connected with the new contact-processes, as will be apparent from the following pages.

The first observation of what we now call "catalytic" or "contact"-reactions, seems to have been made by Sir Humphrey Davy, in 1817. He found that heated platinum wire, introduced into a mixture of oxygen or air with hydrogen, carbon monoxide, ethylene, or cyanogen, increases its heat to a vivid glowing, and that the gaseous mixture is slowly or rapidly burned. In 1820 Edmund Davy found that platinum black, obtained by precipitating a platinum solution with hydrogen sulphide, treating the precipitate with nitric acid, evaporating the solution, and boiling the residue with alcohol, when moistened with spirit of wine, glows up in the air with combustion of the spirit. In 1822 Doebereiner found that the residue produced by igniting ammonio-platinum chloride, when moistened with alcohol, in the air behaves in the same manner; and in 1823 he found that finely divided platinum inflames a current of hydrogen, directed upon it in the presence of air, upon which reaction he founded, in 1824, his celebrated inflaming-machine.

Although the terms "contact" or "catalytic" reactions were :

not used at that time, it is worthy of notice that, soon after Doebereiner had discovered what we now call the contact reaction of platinum in effecting the union of oxygen and hydrogen, Dulong, Thénard, and Dumas found that a number of other substances, both simple and composite, had the same effect; and the notion soon gained ground that these substances owe their function to their porous properties by which gases are condensed within the pores to a small volume, and the molecules are thus brought more nearly together, so that they can react more easily upon each other.

In 1835, Berzelius (*Jahresber.*, xv., published in 1836, pp. 237 *et seq.*) comprised the just mentioned reactions in the same group with a number of reactions observed in organic chemistry (the conversion of starch into sugar by dilute acids, the fermentation of sugar by yeast, the production of ethylic ether from alcohol by strong sulphuric acid), also with the decomposition of hydrogen peroxide by a number of substances, all of them apparently caused by a certain body which remains unchanged and does not itself take part in the new combinations. Berzelius more especially refers to the celebrated investigations by Mitscherlich on the action of sulphuric acid in the formation of ether from alcohol; the terms "contact-substance" and "contact-reactions" indeed were first used by Mitscherlich. Berzelius, however, went further and attributed the above, and all analogous reactions, which he calls "catalyses," to a new "catalytic force" which he does not define very clearly.

We must here mention that Berzelius in the work just quoted does not refer to the contact action of platinum on the union of sulphur dioxide and oxygen, although this fact could hardly have been unknown to him. We shall enter into the general subject of catalysis later on.

Several years before Berzelius published the above generalisation, a fundamental invention had been made which applied to what was afterwards called the catalytic action of platinum in the preparation of sulphur trioxide from dioxide and atmospheric air. The B. P. 6096 (21st March 1831), by Peregrine Phillips, junior, of Bristol, vinegar manufacturer, describes "Certain improvements in manufacturing sulphuric acid, commonly called oil of vitriol, viz., firstly, causing an

instantaneous union of the sulphurous acid gas with the oxygen of the atmosphere, and so save saltpetre and the cost of vitriol chambers, by drawing them in proper proportions, by an air-pump or otherwise, through an ignited tube or tubes of platina, porcelain, or some material not acted on by heated sulphurous acid gas, in which are fine platina wire or platina in any finely divided state. The sulphuric acid formed is absorbed in a lead-lined tower, filled with pebbles over which water is made to trickle down."

Undoubtedly we have here the fundamental features of the contact-process as now employed, and Peregrine Phillips must be called its inventor in the same way as Dyar and Hemming are the inventors of the ammonia-soda process. The history of both inventions presents some common features. Made and patented in England, within a very few years of each other, by persons otherwise absolutely unknown, evidently neither trained chemists nor practical manufacturers in their respective lines, they remained almost unnoticed in the country of their birth; they were taken up in foreign countries, at first by men of science, afterwards by manufacturers, but only after having suffered many checks were they brought to full technical success, both abroad and in England, after an almost equally long interval, during which all attempts in that direction were judged hopeless.

Almost immediately after the publication of Phillips's patent, two German scientists repeated his experiments. Magnus (*Pogg. Ann.*, 1832, xxiv. p. 610) found that 2 vol. sulphur dioxide mixed with 1 vol. oxygen (or more slowly with the corresponding quantity of air) is gradually condensed into sulphuric acid in the presence of water, but much more quickly in the presence of heated platinum, especially in the spongy state. Magnus also observed the formation of a little sulphuric acid on conducting the gaseous mixture through a darkly red-hot tube containing broken glass. At the same time Doebereiner (*ibid.*, p. 609) mentions that he had succeeded in condensing a mixture of 2 vol. sulphur dioxide and 1 vol. oxygen by the assistance of "hygroscopically moist" platinum black to fuming sulphuric acid. (The formation of what we now call "sulphuric anhydride" had been also noticed by Phillips and Magnus.)

A. W. Hofmann, in his Report by the Jury on the Exhibition of 1862, p. 9, mentions a patent of Kuhlmann's, bearing upon the use of platinum as contact-substance for converting  $\text{SO}_2$  into  $\text{SO}_3$ , dated 22nd December 1838. There is no English patent of this kind; probably it was a French patent.

In 1847 it became first known that a Belgian chemist, Schneider, had worked on "the manufacture of sulphuric acid and its concentration to  $66^\circ \text{Bé}$ . without lead chambers and platinum still by a contact-process." The first communication appeared in *Dingl. polyt. J.*, cvi. p. 395; further communications, all from French sources (*Comptes rend.*, *Moniteur universel*, *Bulletin de la Société d'Encouragement*), in the same journal, cvii. pp. 159 and 362, and cix. p. 354. The last is the most extended and contains both a description and somewhat detailed drawings of his apparatus. Schneider showed his process first to a number of Belgian gentlemen (among them Chandelon), afterwards to a committee appointed by the French Academy of Science, to which belonged Dumas, Pelouze, and Payen. Their report (by Payen) testifies that the process had been demonstrated by a model—that, in fact, sulphuric acid had been made without nitric acid or a nitrate, with a yield approaching that obtained in the actual manufacture (by the lead-chamber system), and much greater than was attainable on the small scale without the action of porous bodies. Schneider employed as contact-substance pumice, prepared in a manner which he kept secret even before the examining committee, and which has never been divulged, so that we do not know whether his pumice was platinised (which is the most likely assumption) or treated in any other way; his apparatus (which does not appear to have advanced beyond the stage of a working model) required, for the treatment of 800 kg. sulphur per diem, the considerable space of 500 cb.m., with a contact-surface of 9500 sq. m.

Schneider reports that already twelve years before, in March 1835, Clément-Desormes wrote to him as follows:—"I am convinced that in at most ten years it will be possible to make sulphuric acid on the large scale from its constituents without lead chambers, nitric acid, or nitrates." But that was a wrong prediction, and at all events was never realised "on the large scale" by Schneider, of whom the world has never heard

anything since. We find no mention of *fuming* sulphuric acid in his publications.

*Platinum* in some shape or other has been alluded to by many inventors since Phillips. Already in 1846 (B. P. 11425) J. T. Jullion mentions 'platinum sponge or "asbestos coated or covered with platinum" or other "catalytic or contact-substances" heated to from 600° to 900° F. (316° to 482° C.); but he applies this only to the conversion of nitrogen oxides into "hyponitrous, nitrous, or nitric acid," and to that of hydrochloric acid vapours, by means of oxygen or air, while he makes sulphuric acid from water, sulphurous acid and chlorine without platinum. But a few years later we find platinised asbestos clearly indicated for the manufacture of sulphuric acid.

In 1852 Petrie (B. P. 590) mentions, besides siliceous matter and spongy platinum, also "filaments of asbestos coated with platinum." And in a specification, No. 188 of 1854 (not carried beyond provisional protection), W. H. Thornthwaite speaks of manufacturing sulphuric acid by carrying the vapours of sulphurous acid and the requisite quantity of common air, or passing the fumes from a burning mixture of sulphur and nitrate of potash, over a heated catalysing agent, "by which a considerable saving of nitrate of potash is effected." As such "catalysing agents" he specifies "*platinised asbestos* or other platinised substance not liable to change from the action of sulphuric acid, or the sesquioxide of chromium, of iron, or other sesquioxide."

In 1855 (Liebig's *Jahresber.*, 1855, p. 308) Piria describes the preparation of *anhydrous* sulphuric acid by means of platinised pumice from  $\text{SO}_2$  and air, or preferably oxygen. He had evidently been working entirely on a laboratory scale, but it is interesting to note that his special object was the preparation of sulphuric anhydride, not of ordinary acid, as most of the other inventors had in view.

Already Magnus, as we have seen, had united  $\text{SO}_2$  and O by another "contact-substance" than platinum. In 1848 (B. P. 12264) Læning applied for this purpose pumice-stone, prepared by boiling it in concentrated sulphuric acid, immersing in water containing a little ammonia, drying and heating in a closed retort to near 600° F. (316° C.) with about 1 per cent. of peroxide of manganese, and allowing it to cool out of contact.

with the atmosphere; he describes the product as a "catalytic porous body." The "sulphurous-gas is mixed with a due proportion of atmospheric air and a minute quantity of ammonia gas" (!), and is passed through vertical columns filled with the catalytic body and kept between  $550^{\circ}$  and  $600^{\circ}$  F. ( $288^{\circ}$  to  $316^{\circ}$  C.); the sulphuric acid formed therein is washed out of the columns by water, a chimney maintaining a current throughout the whole conduit.

The next publication to be noticed is by Blondeau (*Comptes rend.*, 1849, xxix. p. 405). Starting from an observation made by Boussingault on the formation of sulphuric acid in some American rivers, near which the gases from burning sulphur ores came into contact with argillaceous sand and schist, Blondeau passed a mixture of sulphur dioxide, air, and steam through a red-hot porcelain tube filled with argillaceous sand, no doubt also containing ferric oxide. He obtained some sulphuric acid, but this was not followed up.

A few years later a very important further step was made for the introduction of other contact-substances than platinum. Wochler and Mahla found in 1852 (*Ann. Chem. Pharm.*, lxxxii. p. 255) that the *oxides of copper, iron, chromium*, best of all a mixture of chromium and copper oxide, brought to a low red-heat, caused the formation of thick fumes from a mixture of  $\text{SO}_2$  and O. Platinum as sponge and sheet did not act at ordinary temperatures; but it acted far below red-heat, copper sponge only after superficial oxidation. Woehler's results gave an impetus to several trials at factories (for instance, at the Oker works), which, however, remained fruitless (Wagner's *Jahresber.* for 1859, p. 144), because the time required for the reaction was too considerable. I have made inquiries about the Oker trials in trustworthy quarters, which have shown, from official sources, that the experiments made there were performed in an iron tube, with a mixture of sulphur dioxide and air, and led to the condensation of acid of 5° Bé. in a lead tube fed with water. Evidently it was only a large scale laboratory experiment.

Woehler and Mahla already gave what is probably a correct interpretation of the catalytic action in this case, viz., the alternate reduction of  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  to  $\text{Fe}_3\text{O}_4$  and  $\text{Cu}_2\text{O}$  by  $\text{SO}_2$ , and their reoxidation by the oxygen; they also noticed that the formation of  $\text{SO}_3$  took place without the presence of



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moisture ; but as the attempts at utilising the reaction on the large scale were made with a view of manufacturing ordinary sulphuric acid, there was probably no attempt made at excluding moisture, which is very prejudicial in this case, as we shall see.

Very soon after Woehler and Mahla's publication, Robb took out two B. Ps. (731 and 788 of 1853), in which he describes the manufacture of sulphuric acid by passing sulphurous acid from pyrites-kilns over peroxide of iron, resulting from the combustion of pyrites, heated to dull red-heat in a furnace or kiln kept hot by the pyrites-gases themselves, air being admitted at the bottom of the kiln. In his second patent he also mentions oxide of manganese and other substances, the whole to be coarsely powdered and made up into bricks, by means of clay or small coal, etc., dried until they are hard. As we have seen above, Thornthwaite in 1854 also mentions the oxides of chromium and iron.

Trueman (B. P. 282 of 1854) makes sulphuric acid from pyrites-kiln and other gases both by the help of platinum (either in the shape of wire or of pumice-stone or other porous substances impregnated with platinum chloride and ignited) and oxides of iron, copper, chromium, and manganese, broken into small lumps and kept at a red-heat. Thornthwaite's B. P. 254 January 1854, contains nothing new.

Schmersahl and Bouck (B. P. 183 of 1855) employ for the manufacture of  $\text{SO}_3$  a mixture of sulphurous acid and air, passed through heated tubes, supplied with asbestos, or a mixture of copper and chrome oxides, platinum in wire or sheets, prepared pumice-stone, coke, animal or other charcoal, or other porous substances which afford an extensive surface. The gases are first passed through water previously to being combined with atmospheric air.

*Silica* is also mentioned as a catalyser for the formation of anhydrous sulphur trioxide ; but the British patents quoted in support of this do not refer to this subject. Thus Petrie (B. Ps. 590 of 1852 ; 2095 of 1856) passes the gases from burning sulphur through towers filled with pebbles ; but as these are to be fed with water, there is no question of "contact-action" as at present understood. W. Hunt (B. P. 1919 of 1853) employs chambers or flues filled with pebbles or pumice or any other

material capable of resisting the action of heat and acid, made nearly red-hot by the heat of the burner-gases or by the spare heat from coke-ovens and the like. "By this means part of the sulphurous acid gas is made to take up oxygen from the air more readily than when the gases are comparatively cool." The sulphuric acid formed is carried forward with some sulphurous acid into a vitriol-chamber or into a condensing-tower fed with nitrosulphuric acid. Evidently Hunt did not contemplate a catalytic action in the proper sense (although this might occur to a slight extent), but merely the promotion of the union of  $\text{SO}_2$  and O by the action of heat.

Plattner (*Die metallurgischen Röstprozesse*, Freiberg, 1856, pp. 334 *et seq.*) tried to carry out Hunt's proposal at the Muldenröhre at Freiberg in such a manner that no fuel is required for keeping the silica serving as contact-substance in the hot state. He arranged two vertical flues within the roasting-kiln or heap, filled with lumps of quartz or siliceous slate, and made the roasting-gases pass through these flues. We may disregard the results obtained by analysing a sample of gas drawn through caustic-potash solution, as this method yields altogether erroneous results, the sulphide in alkaline solution being quickly oxidised by the free oxygen present; but although, on the strength of these analyses, Plattner assumed that a large proportion of  $\text{SO}_2$  had been oxidised to  $\text{SO}_3$  (in one instance 30 : 1!), and says that further experiments were to be made, no practical results have become known, and we may well imagine that the real formation of  $\text{SO}_3$  was ultimately found to be too slight to be of any practical use.

Cl. Winkler, in his paper quoted p. 1286, mentions that Reich, in a pamphlet on the steps taken for dealing with the noxious vapours at the Freiberg works, speaks of experiments made on the same line as Plattner's, but that the effect was much too slow for practical use. Since Reich presumably used the same faulty analytical method as Plattner had done before him, we may take it that there is really nothing certain known about the contact-action of silica, except that it is altogether insufficient for our present purpose.

Henry Deacon, the inventor of the celebrated chlorine process which bears his name, and which is based on the catalytic action of cupric sulphate, or chloride, tried to apply

this action (of course in this case that of the sulphate) to the manufacture of anhydrous or ordinary sulphuric acid (B. Ps. 753 and 1682, both of 1871). Evidently he had no practical success in this direction, although his own energy and that of his gifted collaborator, Dr Hurter, were sufficient to overcome any accidental difficulties. But it is interesting to note that he made two observations, important even to this day, viz.: that any *too sudden cooling* of gases after their treatment in the contact-apparatus should be avoided, and that the reaction goes on more favourably if an *excess of air or oxygen* is employed. His instruction as to the best temperature for the contact-process is certainly too vague to do much good, viz., "between that point at which sulphate of copper begins to be decomposed in a current of hot air and about that point at which tin melts." Another patent of his (1908 of 1871) describes how the  $\text{SO}_3$  formed by passing pyrites burner-gas, mixed with heated air, through a heated vessel containing burnt clay impregnated with a salt of copper is to be mixed with more air or oxygen and is to be made to act on  $\text{NaCl}$  or  $\text{KCl}$ , in order to produce alkaline sulphates and free chlorine.

Up to the time to which we have now arrived in our historical survey, nearly all the attempts at uniting sulphur dioxide and oxygen by contact-processes had aimed at replacing the ordinary lead-chamber process, principally with a view of saving the great cost both of the plant and the nitre, which at that period was many times larger than it is at present, partly owing to the absence or imperfection of nitre-recovery apparatus, partly to the much higher price of nitrate of soda. Several of the inventors certainly speak of fuming sulphuric acid or of sulphuric anhydride, as we have seen, but none of them except Piria (who evidently thought only of laboratory work) places this in the foreground, for the simple reason that there was no market for large quantities of fuming sulphuric acid, and the requirements of the world, at that time, were easily met by the Bohemian works, which could have supplied considerably more of that article, if it had been called for, at such a low cost that competition by the contact-processes, in the imperfect state then known, would have been very difficult.

Just for this reason the various inventors took no special care in excluding moisture in their experiments, if they did not

actually introduce water or steam on purpose; and precisely this circumstance caused the catalytic action to be very slow and imperfect, as moisture (at least when exceeding an extremely small quantity) seems to act as a "poison" for most of the reactions in question. Nor was it sufficiently known up to that time (and much later) what great importance the complete removal of flue-dust and other impurities has for these processes, more particularly those employing platinum. This was first sufficiently proved in the year 1898 by the patents of the Badische Fabrik. Last, not least, the development of chemical engineering was not sufficiently advanced to enable the manufacturer to transfer results gained in the laboratory to the large working scale as easily as this is the case at present. We surely need not wonder at the length of time which elapsed from the date of Phillips's patent to the actual introduction of the contact-process in our industry, if we consider that the working out of the ammonia-soda process to a real going affair did not require much less time.

The first of the above-named reasons for the slow development of the contact-processes, viz., the want of an extensive market for fuming sulphuric acid, was removed through the invention of the synthetical production of alizarine (which became a technical fact about 1872, having been first discovered in December 1868), and of other colouring-matters, equally requiring at intermediate stages of the manufacture the preparation of sulphonic acids, not obtainable except by the agency of fuming sulphuric acid. The demand for that article rapidly rose to such an extent that the Bohemian works founded upon the exploitation of "copperas-slate," all of which then belonged to the firm of J. D. Starck, could hardly supply it, and the naturally greatly enhanced price made this situation even more unbearable to the manufacturers of tar-colours. Many chemists at that period turned their attention towards the production of fuming sulphuric acid in other places and by other methods, either in the direction of carrying out the Bohemian process with some other and more suitable material than the Pilsen slates, or in that of applying one or more of the contact-processes invented from the time of Phillips onwards.

We have already mentioned (pp. 1264 *et seq.*) the attempts in the former direction, which have all failed in the long run,

and we now turn to the second class of processes. It is worthy of remark that the foundations had been laid long before by Phillips's patent for making sulphuric anhydride by the contact-process, and that only platinum and ferric oxide (which were used at a very early period), but no new catalysers, have come into practical use for manufacturing purposes up to the present time, as far as can be judged in the face of the great secrecy observed by most factories just on this point, in spite of the great number of contact-substances discovered since that time. To be sure, the recognised fact that for the platinum process *all* impurities, especially arsenic, must be removed, and that the heat of reaction is injurious and must be carried away, belongs to a later period and did not become known before the patents of the Badische Fabrik. But just that proposal which, at the turning-point at which we have now arrived, aroused the greatest attention, and professed both to explain the mishaps of former inventors and to usher in a period of more successful working, viz., the exclusion of an excess of oxygen as well as of inert gas, has proved to be a step in the wrong direction, which has caused the waste of very much time, energy, and money. Indirectly, however, it has been very useful in imparting fresh courage to those working in that field, and in first placing synthetically produced fuming sulphuric acid into the market.

The publication of Clemens Winkler's paper in *Dingl. polyt. J.*, October 1875, vol. ccxviii., p. 128, is universally acknowledged to have been the opening of a new epoch in the history of the manufacture of fuming sulphuric acid, nay, although nobody dreamed of it at the time (as it has turned out), in that of sulphuric acid generally. That this was "in the air," that the practical introduction of contact-processes from one side or another was only a question of time, need not be said, and is best proved by the fact that almost on the same day that Winkler sent his manuscript to Dingler, W. S. Squire lodged an application for a B. P. (3278 of 18th September 1875), which, strange to say, embodies precisely the same idea (now known to be erroneous) concerning the best composition of the gases for the contact-process and the way of securing this composition by decomposing sulphuric acid itself by strong heat. This process was the common

invention of W. S. Squire and Rudolph Messel. The two authors a little later (20th April 1876) read a paper concerning their process before the Chemical Society, but it does not appear in its *Transactions*. I am, however, enabled, by the kindness of Dr Messel, who has sent me a manuscript copy of that paper, to quote a few points of historical interest from it. The inventors were, like Winkler, induced to try the catalytic process by the sudden rise in the price of fuming oil of vitriol, and they tested the action of pumice impregnated with a solution of platinum chloride and ammonium chloride, heated to dull redness, on a mixture of the vapours of burning sulphur and air, or of SO produced from copper and sulphuric acid, with just enough air to oxidise the SO<sub>2</sub>. Dense clouds of SO<sub>3</sub> were at once observed, but could not be properly condensed. This was, however, possible when passing a mixture of pure SO<sub>2</sub> and oxygen in the requisite proportions over spongy platinum. "The whole, or very nearly the whole," of the SO<sub>2</sub> was oxidised, and in the absence of foreign gases the condensation of liquid SO<sub>3</sub> was "extremely perfect." The next step was to prepare the mixture of SO<sub>2</sub> and O on a commercial scale; and the inventors, like Winkler, bethought themselves of Deville's celebrated process of preparing oxygen by subjecting sulphuric acid to a high temperature. They boiled strong sulphuric acid in a small platinum still, passed the vapours through a platinum tube kept at nearly white-heat, cooled and dried the vapours issuing from that tube, and passed them through a second tube containing platinised pumice kept at a dull red-heat. Thus they obtained nearly 70 parts of SO<sub>3</sub> from 100 parts of white sulphuric acid.

They further tried Woehler and Mahla's mixture of the oxides of chromium and copper, made into pills with asbestos and heated to redness; but they preferred to employ spongy platinum in an apparatus erected at Silvertown, capable of producing some tons of anhydrous SO<sub>3</sub> per week, which was nearly ready for starting at that time (April, 1876). They ultimately note that the loss of activity of the catalytic agent is due to the accumulation of foreign matter, such as flue-dust, which would not exist in their process of preparing the mixture of SO<sub>2</sub> and O from strong sulphuric acid. (Arsenic, however, is not mentioned here, and the importance of excluding even the

smallest traces of volatile arsenic compounds as a "contact-poison" was evidently quite unknown at that time.)

Winkler's paper of 1875 deals firstly with the imperfections of the Bohemian process and the attempts at making it generally accessible by reconvertng the ferric oxide into sulphate by means of ordinary sulphuric acid (*cf.* p. 1265), which do not remove the principal objections to that process. He then turns to the attempts at the synthesis of  $\text{SO}_3$  from  $\text{SO}_2$  and O by contact-substances, among which platinum in a finely divided state is the most efficacious. The platinum should be spread over as great a surface as possible, and so-called platinised asbestos has been especially recommended for this purpose. [As we see, Winkler does not claim to have first proposed platinised asbestos, which had long before been used by Jullion, Petrie, and Thornthwaite, p. 1280.] Pumice or porous porcelain are much less efficacious [*cf.* below, Winkler's later experience, contrary to the above]. The action of platinised asbestos is, however, very different according to the state of dilution of the gases. In a mixture of pure  $\text{SO}_2$  and pure O, 73.3 per cent. of the  $\text{SO}_2$  was converted into  $\text{SO}_3$ , in a mixture of pure  $\text{SO}_2$  and air only 47.4 per cent., and in a gas produced by burning sulphur in air, and containing 4 or 5 per cent.  $\text{SO}_2$ , only 11.5 per cent. Winkler concluded from this that the action of contact-substances is diminished by the presence of inert gases, and, as a matter of course, an excess of sulphur dioxide or oxygen remains indifferent, and therefore acts as a diluent. Hence the two gases should be employed in the exact stoichiometrical proportion, in which case only can we expect a quantitative conversion of  $\text{SO}_2$  into  $\text{SO}_3$ . [This reasoning is in contradiction to the law of the action of masses, which was almost unknown to chemists or at least hardly regarded by them at that time, and it has been recognised as erroneous by Winkler himself and everybody else: *cf.* Deacon, p. 1283.]

\* In order to obtain such a stoichiometrical mixture of pure  $\text{SO}_2$  and O, without diluent gases, in the exact proportions, Winkler proposes to make use of the well-known fact that ordinary concentrated sulphuric acid is by strong heating decomposed into sulphur dioxide, oxygen, and aqueous vapour; the latter is completely condensed and removed by absorption in strong sulphuric acid, and the remaining dry mixture of  $\text{SO}_2$

and O exposed to the action of platinised asbestos at a low red-heat ("gelindes Rothglühen"). He describes a laboratory experiment made on those lines, in which 93 per cent. of the strong sulphuric acid was decomposed and 78.4 per cent. of the decomposed acid (or 73.7 per cent. of the total acid employed) was converted into  $\text{SO}_2$ . On this he founded proposals for carrying out the process on a large scale which we need not repeat, as that process soon after was recognised as too expensive, perhaps first of all (as we now know) by the inventor himself.

(We must notice here that the yield of  $\text{SO}_2$  found by Winkler, although it seemed encouraging enough at a time when only the manufacture of fuming acid was thought of, and when that acid cost many times as much as ordinary sulphuric acid, would be called at the present time much too low even to pay for fuming acid. Of course longer practice would probably have led to a somewhat better yield, but we now know from theoretical considerations that the maximum yield obtainable from  $\text{SO}_2$  requires the employment of *more* than the stoichiometrical proportion of oxygen.)

Winkler also mentions the possibility of the contact-action of platinum being destroyed in course of time; but this, he says, can be caused only by flue-dust and other extraneous impurities, which are excluded in his process of obtaining the gaseous mixture by decomposition of sulphuric acid.

A little later (*Dingl. polyt. J.*, 1877, ccxxiii. p. 409) Winkler still defended his process against the objection of Debray, according to whom the decomposition of sulphuric acid requires too high a temperature and causes a rapid destruction of the apparatus, whether made of metal or earthenware; but very soon after, as we shall see later on from his own statement, he must have convinced himself that Debray's objections were only too well founded.

The publication of Winkler's paper acted upon the industrial chemical world like a sorcerer's wand upon pent-up spirits. The fatal spell hitherto resting upon the synthesis of sulphur trioxide by catalytic action seemed to be broken; the relieving word seemed to have been found, which explained all the miscarriages of former inventors, viz., that pure sulphur dioxide and pure oxygen should be present in the theoretical proportion



without an excess of either or any inert gases; and although the method of securing this, the splitting up of sulphuric acid, was evidently too expensive and could of course never be dreamt of for the manufacture of ordinary sulphuric acid itself, this did not debar the expectation that the new process would break the monopoly of the Bohemian works for that expensive article, *fuming* sulphuric acid.

In Great Britain certainly Squire's patent barred the way except for the firm to which the patent belonged; but in Germany the road was free, as the patent law for the German Empire was only introduced in the following year, and Winkler had not taken out patents for the single German states. Any number of chemists in that country, where the sudden expansion of the coal-tar colour industry made the want most urgently felt, threw themselves upon this promising path. It is curious to notice that precisely the want of patent protection for Winkler's process, much as it stimulated the efforts of other chemists in one way, had a harmful effect in another direction. Just because no patent stood in the way, a number of factories sprung up in Germany for the purpose of carrying out Winkler's process, and all efforts were directed towards overcoming the technical difficulties of decomposing sulphuric acid into  $\text{SO}_2$ ,  $\text{O}$ , and  $\text{H}_2\text{O}$ , which are caused by the very high temperature required for this reaction, and the immense corrosive action of the substances in question on the material of the apparatus. It took much time, labour, and capital before it was recognised, both that this part of the process was much too difficult and expensive for practical purposes, and that it was worse than unnecessary even to aim at producing an exact mixture of 2 vol.  $\text{SO}_2$  and 1 vol.  $\text{O}_2$ . If other chemists had been compelled, by the existence of a patent for Winkler's process of 1875, to turn their attention in another direction, their labours would have been much sooner rewarded with success. The loss of time and trouble in this matter is very strongly expressed by Ostwald (*Z. Elektrochem.*, 1902, viii. p. 154), who says that every chemist acquainted with Guldberg-Waage's law might, a quarter of a century ago, have read the fallacy of Winkler's reasoning from the equation of the reaction. But it is only just to Winkler to point out that in 1875 and very much later hardly any chemist, scientific or practical, did pay attention to

Guldberg-Waage's law in his reasoning. Winkler's paper notoriously at once roused quite as much attention among purely scientific as among practical chemists. Probably every professor of chemistry has mentioned it in his lectures from that time to the present, and most of them have demonstrated his experiment in their lectures. Why was Winkler's reasoning never protested against, as contrary to the above law, until Knietsch did so in 1901? Nobody can blame Winkler for his mistake in neglecting that law in 1875, a mistake which practically every professor of chemistry has committed who has quoted his work without criticism, as they all did during many years. Winkler indeed was quite in the right when trying to exclude nitrogen as an injurious diluent, and he erred only in considering any oxygen present over and above the stoichiometrical proportions as an equally injurious diluent.

One of the first who recognised the fact that the preparation of a mixture of exactly 2 vol.  $\text{SO}_2$  and 1 vol.  $\text{O}_2$ , without any other gases, was unnecessary, and, as we now know, not even suitable for the purpose in question, was Winkler himself, as we shall see later on; but this remained a profound secret for many years, up to 1900, and during the first few years after 1875 the original Winkler process, based on the decomposition of sulphuric acid into  $\text{SO}_2$ ,  $\text{O}$ , and  $\text{H}_2\text{O}$  at a very high temperature,<sup>1</sup> ruled the exertions of most or all German chemists. A number of factories founded upon that process soon sprang up, as there was an enormous margin between the cost price of fuming O.V. and its selling price at that time (2s. 6d. per kg. of  $\text{SO}_3$  contained in fuming O.V.). The monopoly of the Bohemian works was thus broken.

I cannot ascertain when the first fuming acid made by synthesis at the Silvertown works came into the market. In Germany this was undoubtedly the acid made by Dr Adolph Clemm in 1877, as mentioned p. 1269, by the bisulphate method. Soon after followed Dr Emil Jacob in Kreuznach, who

<sup>1</sup> In Germany the expression "Winkler's process" is frequently, but altogether erroneously, applied to the production of sulphuric anhydride by platinum catalysis generally. Evidently that expression should be confined to that modification of the catalytic process which is mentioned in the text, as published by Winkler in 1875, and simultaneously and independently invented by Squire and Messel.

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apparently worked first by Winkler's method, but later on with gases from burning brimstone.

An authentic report respecting the work carried on in secrecy at Freiberg, from 1877 onwards, will be found later on.

From communications by Dr Emil Jacob, and original documents submitted by him, it appears that he supplied large quantities of 43 per cent. fuming acid to the Höchst works in 1879. In 1880 the yield of such acid, starting with strong sulphuric acid (66° Bé.), was 61.9 per cent., in 1882 already 70.4 per cent. The following cost-sheet for four months, commencing 1st January 1882, even now presents sufficient interest to be reproduced here :—

	Marks.
258,408 kg. acid 66° Bé. . . . .	22,988
32 truckloads coal . . . . .	4,000
Wages . . . . .	3,600
Repairs and replacing apparatus . . . . .	2,800
Amortisation 10 per cent. on 24,000 M. (cost of plant) . . . . .	800
<hr/>	
Cost of 181,990 kg. fuming acid (43 per cent. SO <sub>3</sub> ), with- out packages . . . . .	34,188
Selling price of same . . . . .	67,340
Besides 43 tons weak acid 27° Bé. . . . .	

On 17th August 1882, Dr Jacob sold his process, which was at that time the same as the Winkler process of 1875, to Messrs Meister, Lucius, & Brüning, who forthwith introduced it at their Höchst works. But in 1886 he started working with pyrites-gases, and in 1887 with brimstone-gases, which answered very well.

About that time the Ludwigshafen factory of the "Badische" commenced work, but the precise time does not appear clearly from the statements of Knietsch (*Ber.*, 1901, p. 1477).

At nearly the same time the Thann Chemical Works, in Alsace, proceeded on other lines. The following communications as to their hitherto entirely unknown doings are due to the kindness of M. Meunier-Dollfus, the surviving partner. In September 1878 the above firm made a contract with the firm of Chapman, Messel, & Co., of London and Silvertown, for the purchase of the process patented by W. Squire in 1875 and following years, founded (like Winkler's process) on the decomposition of strong sulphuric acid by heat. While the

preliminary researches were going on for adapting and installing that process at Thann, Mr Squire, who had in the meantime severed his connection with the London firm, offered to the senior partner of the Thann firm, M. Scheurer-Kestner, a new process invented by him, as being greatly superior to the process then at work at Silvertown. It was resolved, in accordance with the London firm, to study the new process and to introduce it at the Thann works as soon as possible. These studies commenced in April 1879, and after gradually overcoming manifold difficulties, they led to a very satisfactory solution of the problem. Sicilian sulphur was burnt in the usual manner, and the gases were treated with water in a column apparatus under a pressure of 4 atm. The  $\text{SO}_2$  was expelled by steam from the solution thus obtained, then mixed with the theoretical quantity of air and passed over heated platinum asbestos. The  $\text{SO}_3$  formed was absorbed in towers by concentrated sulphuric acid, and fuming acid of 40 per cent.  $\text{SO}_3$  was thus obtained. The exit-gases, still containing  $\text{SO}_2$ , were passed back into the process. The daily make was 30 cwt.  $\text{SO}_3$ , and the yield 90 per cent. of the theoretical. At the beginning of 1881 this process was in regular working order at Thann, and it was subsequently also introduced at Ludwigshafen.

Except what I am enabled to quote from M. Meunier's communication, nothing else is known about the work done at the Silvertown works since 1876, which have certainly been producers of fuming sulphuric acid ever since that time.

The firm of J. D. Starck, when it saw its monopoly broken through in the manner described, combined with the works at Mannheim, Kreuznach, Höchst, and Thann for keeping up the prices of fuming O.V., and this agreement lasted until the Badische Fabrik came into the market with such large quantities that the "combine" gradually dissolved.

The further history of the manufacture of sulphuric anhydride by the contact-process up to 1900 was formerly enveloped in great mystery, but sparsely enlightened by the patents taken out in the meantime, and by a very few glimpses from the practical experiments carried on at various German factories. These experiments were surrounded with all the more secrecy, as there seemed to be so little ground upon which patents could be based after the great number of previous publications on the

subject of contact-processes. This period lasted up to the publication of the first patents of the Badische Fabrik, which usher in a new epoch. What has been done in the meantime is now, to a great extent, cleared up by the publications of Winkler (in 1900), of Knietzsch (1901), and by the special communications which I am enabled to give later on. First, however, we shall follow up what can be gleaned from the patents and a few other notes during the period following the publication of Winkler's first paper.

As previously stated, the first years of that period were mainly spent in attempts to carry out Winkler's process on the large scale. The abandonment of this process was caused by the difficulties mentioned by Debray (p. 1289), especially during the decomposition of the sulphuric acid. The greatest difficulty in Winkler's process for manufacturing fuming oil of vitriol or anhydride, and in all other processes started in consequence of the impetus given by him, is indeed the material of the vessels to be employed. Wallace, in his patent of 30th May 1876, proposed to employ glazed plumbago retorts. Some factories seem to have employed platinum vessels, which are, however, strongly acted upon, as was shown by Scheurer-Kestner. The extent of this action partly depends upon the amount of arsenic and nitrous acid contained in the sulphuric acid (*cf.* Wagner's *Jahresber.*, 1877, p. 238), partly also upon the special construction of the apparatus. According to communications made to me by Dr Majert, the apparatus employed by him at the Schlebusch works, near Cologne, was arranged as follows (*cf.* also his Fr. 1. 122130 of 16th January 1878):—The decomposition of sulphuric acid into  $\text{SO}_2$ , O, and  $\text{H}_2\text{O}$  was effected in upright retorts made of a mixture of three parts burnt fireclay broken to the size of a pea, and one part best Belgian fireclay, and glazed with a mass which at the highest temperature of the process becomes pasty but not liquid, so that any cracks occurring in the retort become filled with the glaze. The retorts were perpendicular, entirely surrounded by the fire, and closed at top and bottom by hydraulic joints. The top joint served for introducing the pipe conveying the acid to be decomposed, the bottom joint for making the sides of the retort tight in the fixed bottom, which is perforated by the pipe which carries off the gases. Both the

"hydraulic" joints, which were entirely surrounded by the fire, were luted with melted glass. Within the first retort there was a cylinder, into which the vitriol flowed from a small platinum tube, so as not to touch the sides of the retort at all. It was thus evaporated within the inner cylinder, and partly decomposed there, partly in the annular space between the cylinder and the retort, and completely in the second retort. The vapour and gases were conveyed from the first to the second retort by a twice-bent tube, which passed through the bottoms of both retorts, and whose horizontal part was surrounded by the flame of the fireplace. The gases passed away from the top of the second retort into a condenser for liquefying most of the water, then into a drying-tower, and at last into the apparatus for uniting  $\text{SO}_2$  and  $\text{O}$ , consisting of cast-iron retorts filled with wire-gauze shelves, upon which the platinised asbestos was spread. (This factory has not been at work for a long time.)

Angerstein (Ger. P. 26959 of 14th September 1883) describes a special apparatus for decomposing the sulphuric acid, which is supplied from below, evaporated in a shallow platinum dish and decomposed in fireclay pipes filled with broken fire-bricks and heated outside to a very high temperature by the combustion of gaseous fuel under pressure.

According to a Ger. P. of Squire's (4285 of 3rd March 1878), strong sulphuric acid is introduced into a red-hot tower packed with hollow bricks and previously filled with dry steam. The sulphuric acid is in the form of a mist, produced by a compressed gaseous mixture of sulphurous acid and oxygen. The products of decomposition are conveyed in a horizontal closed channel through a lead pan filled with dilute sulphuric acid, where the water is condensed by cooling, whilst the heat of the gases concentrates the sulphuric acid contained in the pan and frees it from sulphurous acid. A further condensation takes place in cooling-pipes; and ultimately the gases are dried in a coke-tower by means of strong sulphuric acid, which is again concentrated and freed from  $\text{SO}_2$  in the lead pan just mentioned. The dry mixture of  $\text{SO}_2$  and  $\text{O}$  is combined to  $\text{SO}_3$  in a specially heated apparatus made of cast-iron outside and brick-work inside, fitted with a pyrometer, where it is brought into contact with platinised asbestos, being forced to travel a circuitous path between courses of bricks. The vapour of

anhydride is absorbed by strongest sulphuric acid in a cast-iron tower, fitted with dishes of a peculiar shape, placed one over another. (The specification gives further details and diagrams of the apparatus.)

After a few years the decomposition of sulphuric acid by heat, for the purpose of obtaining a suitable mixture of  $\text{SO}_2$  and  $\text{O}$ , was given up everywhere, owing to the great expense of the process and the extreme wear and tear of the apparatus. But the belief, that the gases should be combined in stoichiometrical proportions and as little as possible diluted with inert gases, was still prevalent and led to a number of attempts at producing the same effect in a cheaper and more practicable way than that indicated by Winkler and by Squire and Messel in 1875. Those proposals which have been made public are the following:—

J. Neale (B. P. 1103 of 14th March 1876) heats anhydrous sulphates or bisulphates of iron, zinc, aluminium, or sodium in earthenware retorts or muffles, and conducts the mixture of sulphurous acid and oxygen formed by their decomposition over heated spongy platinum, or the oxides of chromium, iron, or copper, or any other substance which may cause the mixture to combine into sulphuric anhydride. The latter is then condensed by itself or utilised for fuming oil of vitriol by receiving it into ordinary strong sulphuric acid.

Scheurer-Kestner (*Comptes rend.*, xcix. p. 876) asserts that on heating a mixture of 2 parts of anhydrous calcium or magnesium sulphate with 1 part of ferric oxide to a bright red-heat, all the sulphuric anhydride is driven off, at first as such, afterwards decomposed into  $\text{SO}_2$  and  $\text{O}$ . By mixing 175 parts of gypsum with 100 of fluorspar and ferric oxide, the decomposition takes place at a lower temperature (that of the Bunsen burner) and the  $\text{SO}_3$  is then not dissociated into  $\text{SO}_2$  and  $\text{O}$ .

To avoid the dilution of sulphur dioxide with excess of air and of nitrogen, unavoidable when burning sulphur or pyrites, and which at that time was still considered very injurious for contact-action, Schroder and Haenisch proposed to employ the pure  $\text{SO}_2$  obtained by their process in a somewhat costly manner (p. 534). The application of this to the manufacture of  $\text{SO}_3$  forms the subject of their B. P. 9188 of 1887, which gives the following prescriptions. A mixture of pure sulphur dioxide and air in a certain fixed proportion is passed at a

low red-heat, and under pressure, over platinised asbestos, whereby a large surface and a lengthened duration of contact of the gases are ensured. The pressure also promotes chemical reaction by bringing nearer together the active gas-molecules. A gas-mixture consisting of 25 per cent.  $\text{SO}_2$  and 75 per cent. air is most suitable for the process; the mixing of the gases simultaneously with their compression is effected by a double cylinder compressor, the two cylinders of which have a cross-sectional area in the proportion of 1 : 3, so that one cylinder pumps three times as much air as the other pumps sulphurous anhydride. The compressed gases meet in the conducting-tube and pass into an air-chamber, and thence into the combining-apparatus. This consists of two horizontal wrought-iron tubes, set in a furnace, of somewhat narrow diameter and strong walls, sufficient to stand a pressure of several atmospheres at a dark red-heat; they are filled with platinised asbestos prepared in a special manner. The pressure (usually 2 to 3 atm.) is regulated by a valve at the common exit-tube. Here most of the  $\text{SO}_2$  is converted into  $\text{SO}_3$ ; and lest this should deposit in a solid form in the tubes or in the valve, the parts projecting from the furnace are surrounded by a leaden steam-coil. If, in spite of this, there should be some obstruction by the crystallisation of  $\text{SO}_3$ , the pressure in the air-chamber will raise a valve, weighted about 1 atm. above the exit-valve. From the latter the remaining gases pass through condensing-jars, where the  $\text{SO}_3$  deposits in the solid form or is retained by strong sulphuric acid. The  $\text{SO}_2$  still present is separated from the nitrogen by water and used over again. This process was carried out in one or two places and worked quite well, until the development of the processes dealing with pyrites-kiln gases made it unprofitable (cf. Dr Schroeder's communication to myself later on).

The task was also approved from the other side, viz., excluding the nitrogen of atmospheric air. This was first proposed by Messel (B. P. 186 of 15th January 1878). He prescribes burning sulphur by means of oxygen, obtained by the electrolysis of acidulated water with the help of dynamo-electrical machines. The sulphur dioxide formed, mixed with the excess of oxygen required for forming  $\text{SO}_3$ ,



is conveyed into a gas-holder, from which the gases are carried at a high temperature over spongy platinum, platinised asbestos, oxide of chromium, iron, or copper. The sulphur trioxide formed is condensed by itself or absorbed in sulphuric acid. By employing two gas-holders the process is made continuous. The electrolytical hydrogen formed at the same time is employed for heating, or it is carburetted and employed for lighting. This process must have been too expensive, owing to the cost of electrolytically-made oxygen. When that gas became a cheap commodity through the development of Brin's processes, I myself (B. P. 3166 of 1888, taken out for me by Ellice-Clark) proposed utilising such oxygen in a similar manner, in such a way that no external heat should be required, and there should be no waste gases of any sort. I abstain from giving a detailed description or drawing of the apparatus proposed by me, as it is now certain that the admixture of nitrogen does not, as formerly assumed, prevent the complete oxidation of  $\text{SO}_2$ , provided the contact-substance is sufficiently active; this circumstance deprives the pure oxygen of its advantages in comparison with atmospheric air.

The task of manufacturing sulphuric anhydride in a sufficiently cheap manner could not be regarded as solved until it had been proved that gases from *sulphur-burners*, or, still better, from *pyrites- or blende-burners*, could be employed for this purpose.

Clemens Winkler himself speedily recognised this when trying to carry out his process on the large scale: he had already, about 1877, suggested the employment of pyrites-burner gases, as mentioned by him in 1900 (*Z. angew. Chem.*, 1900, p. 738; cf. a previous notice by myself, *ibid.* p. 80); but this suggestion, as well as its practical pursuit and the partial success ultimately obtained in this direction, remained an absolute secret of the factories at Freiberg and Stolberg. We shall refer to this subject more in detail later on.

In this paper of 1900, Winkler mentions the great difficulties which had to be overcome in purifying the gases from flue-dust, in order to preserve the action of the catalytic substance. These difficulties were, according to his statement, avoided by Jacob, of Kreuznach, through the employment of gases from burning brimstone (cf. p. 1292).

A French patent, not mentioned anywhere in former publications, was taken out by Lange and Göpner (123906, of 16th April 1878), for treating ordinary pyrites-kiln gas (of whose purification nothing is said) by red-hot pyrites-cinders, or platinum sponge, or analogous substances in tubes made of graphite, cast-iron, and the like, in order to produce sulphuric anhydride or fuming O.V. No details are given respecting the apparatus or method, and such a general claim would of course have been quite untenable. No English or German patent exists for this "invention."

In 1878 Messel took out provisional protection (B. P. No. 1201) for making monohydrated sulphuric acid by means of  $\text{SO}_3$  produced by catalytic action from the gases of burning sulphur. This patent was not completed.

The first mention of employing ordinary pyrites-burner gases which I can find in the printed literature since 1875 is the following, much later than (as we now know) the actual work secretly done in that line at several factories.

Rath (Ger. P. 22118 of 1883) passes pyrites-burner gases, to free them from most of the water, through a cooling-apparatus, consisting of a large number of perpendicular lead pipes placed in cold water, at a velocity not exceeding 5 in. per second. Air may be admitted to them by means of a valve. From the cooler the gases pass through a coke-tower fed with acid of 140° Tw. In order to be thoroughly dried here, the velocity of the gaseous current should not exceed  $2\frac{1}{2}$  in. From here the gases are aspirated by a pump and forced through a number of iron retorts, lined with clay, which contain the contact-substance, and are heated to a temperature between dark and bright red-heat. The number and size of these retorts must be chosen in such a manner that the velocity of the gases does not exceed  $2\frac{1}{4}$  in. The sulphuric anhydride formed here is either condensed in the liquid form in tin-plate vessels standing in a place heated to 25° to 30°, or else it is passed into cast-iron vessels charged with sulphuric hydrate and kept at 25°. Special precautions are required for gases containing carbon monoxide or hydrocarbons. According to Knietzsch (*Ber.*, 1901, p. 4078) nothing is known as to the practical success of the above process.

The later history of this part of our subject is contained in

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the various communications given below from the firms now working contact-processes on the large scale.

### *Theory of the Contact-Processes for the Manufacture of Sulphuric Anhydride.*

We have now passed in review the former stages through which the contact-processes in our field have gone. Before proceeding to describe the present state of this industry, we shall interpose an account of the various views respecting the theoretical side of this problem.

We have already (p. 1277) briefly referred to the very indistinct views of Berzelius on contact or catalytic action, and to the ideas concerning a particular class of such action which for a long time were universally accepted, which, however, do not embrace the whole field of catalytic actions, but mainly those where solid porous bodies come into question, which would certainly apply to our present case. But even for this the explanation, according to which those reactions are caused by the condensation of gases within the pores and the greater mutual attraction of their molecules under this condition, is at present held not to be correct or at least not sufficient.

Liebig attempted to explain catalysis in this way: that a substance (the catalyser) whose molecules possess a "chemical motion" may impart that motion to another substance present, and may thus cause a chemical reaction which that substance would not have undergone without the presence of the catalyser. This "explanation" is certainly quite hypothetical and incapable of direct proof; it did not in reality make the matter clearer, nor could it assist in discovering new facts, which is the real test of a "working hypothesis"; but Ostwald is hardly just in saying that Liebig thereby retarded the investigation of the problem of catalysis by half a century. It is a fact that Liebig's explanation was never anything like generally acknowledged among chemists as a true solution of the problem, and it could not therefore retard the progress of science.

Liebig's explanation of catalysis, so far as it went, applied more to the phenomena of catalysis among liquids than to those which interest us in this place, and we will not detain ourselves with it.

A somewhat clearer explanation of catalytic actions has been given by Bunsen, in his *Gasometrische Methoden*, 1st ed. p. 267. According to him, chemical combinations are not dependent entirely upon the mutual attraction of the substances entering into combination, but also upon the attraction of other substances which are present, but do not take part in the combination; in other words, these combinations are the resultant of the attracting forces exerted by *all* the molecules present in the sphere of the chemical action, whether these molecules take part in the combination or not. For instance, the elements composing hydrogen peroxide are capable of uniting in the attraction sphere of water molecules, but not in that of metallic oxides or of platinum. Thus there is some analogy of catalytic action with that of masses, as has been pointed out elsewhere.

Bunsen's theory probably contains elements of truth, but is hardly of a kind to help us understand the special cases under consideration. We may pass over several other physical or mechanical theories of catalysis (*cf.* Fehling's *Handwörterb. der Chem.*, iii. p. 945) and turn to the chemical theory of catalysis.

Ostwald (*Grundriss der allgemeinen Chemie*, 3rd ed. p. 515) explains a catalyser as a substance which, without appearing among the final products of a reaction, alters its velocity. He has (*cf.* p. 1008) applied this even to the manufacture of sulphuric acid by the vitriol-chamber process. He says: "Sulphur dioxide is oxidised by air and water alone to sulphuric acid, but very slowly; the presence of nitrogen oxides merely hastens this process." Nobody will or can deny this, but Ostwald, as we have seen (p. 1009), seems to go too far in neglecting the importance of the intermediate reactions as if they were unessential and accidental. Quite the contrary, the investigation of these intermediate reactions seems to be a step towards a *real* explanation of the otherwise enigmatic "change of velocity" of the reaction in question.

Evidently even in the case of platinum as a catalyser, one of the simplest cases of catalytic action, the formula of Ostwald is too simple and cuts the knot instead of untying it.

This seems to be confirmed by the behaviour of another catalytic substance which comes into play in this our present subject, viz., *ferric oxide*. This agent may be taken as playing

an intermediate part between the action of platinum and that of the nitrogen oxides. It is a solid substance of porous nature, not known to be particularly active in condensing gases by its physical character (let alone liquids!), and it acts only at a high temperature on a mixture of  $\text{SO}_2 + \text{O}$ , similarly to platinum. But, on the other hand, it does form a compound with the product of the reaction; this compound,  $\text{Fe}_2(\text{SO}_4)_3$ , exists as such at comparatively high temperatures, viz., just below a dark red-heat, and decomposes again into  $\text{Fe}_2\text{O}_3$  and  $3\text{SO}_3$  at a temperature not far removed from that which has been observed as the optimum for the "catalytic" action of ferric oxide. Here the explanation of the catalytic action seems to be this: by the interaction of  $\text{Fe}_2\text{O}_3$ ,  $\text{O}$ , and  $\text{SO}_2$ , many molecules of  $\text{Fe}_2(\text{SO}_4)_3$  are formed, but as the temperature at which this compound is split up into  $\text{Fe}_2\text{O}_3$  and  $3\text{SO}_3$  is very nearly the same as that at which it has been formed, that splitting up actually takes place,  $\text{SO}_3$  is removed in the state of vapour, and  $\text{Fe}_2\text{O}_3$  is again at disposal for combining with  $\text{SO}_2$  and  $\text{O}$ . This explanation deals with reactions and substances actually and easily observed, and we have a right to assume that it certainly does come into play, a state of equilibrium being established for each temperature, in which a certain number of molecules of  $\text{Fe}_2(\text{SO}_4)_3$  are formed and others are split up into  $\text{Fe}_2\text{O}_3$  and  $3\text{SO}_3$ . At the same time another set of reactions is possible and indeed quite as probable to take place, although the conditions of equilibrium may here lead to a different optimum of temperature. These are the reactions: (1)  $3\text{Fe}_2\text{O}_3 + \text{SO}_2 = 2\text{Fe}_3\text{O}_4 + \text{SO}_3$ , and (2)  $2\text{Fe}_3\text{O}_4 + \text{O} = 3\text{Fe}_2\text{O}_3$ .

Precisely in the same way the catalytic functions of chromium oxide, of cupric oxide, sulphate, or dioxide, and all other substances can be explained which are subject to easy changes of valency, and therefore form two or more sets of compounds with oxygen, chlorine, or acid radicles.

A very interesting paper by Manchot and Wilhelms (*Berl. Ber.*, 1901, p. 2479) shows that the catalytic action of the salts of iron may be due to the intermediate formation of a peroxide,  $\text{FeO}_2$ ; but as their work extended only to reactions in the wet way, we cannot take it into account for our present purpose.

I myself, in *Z. angew. Chem.*, 1902, p. 149, explain the catalytic

action of  $\text{Fe}_2\text{O}_3$ , as due, firstly, to the successive reduction of this oxide by  $\text{SO}_2$  to  $\text{Fe}_3\text{O}_4$ , with formation of  $\text{SO}_3$ , and the re-oxidation of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  by free oxygen; secondly, to the simultaneous fixation of  $\text{SO}_2$  and O in the form of  $\text{Fe}_2(\text{SO}_4)_3$ , and the splitting up of this into  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$ .

Keppeler (*ibid.*, 1902, p. 809) assents to this. He also caused one of his students, J. d'Ans, to work on the  $\text{SO}_3$  tensions of ferric sulphate. Their common work is published in the dissertation of d'Ans, Kiel, 1905, in *Z. physik. Chem.*, 1908, lxii. pp. 89 to 118, and in *Z. angew. Chem.*, 1908, pp. 532 to 546 and 577 to 589.

Most or all chemists have thus recognised the existence of intermediate reactions in the case of ferric oxide and similar oxides as catalysers (cf. *e.g.* Wochler and Mahla, p. 1281), but the majority of chemists preferred to consider the action of platinum, which is so manifestly aided by its division over great surfaces, as different from the former class of processes. Platinum was generally regarded as having no affinity for oxygen at the temperature of the reaction, and as acting merely by condensing gaseous bodies in its pores. But there were always chemists who believed in the transitory formation of platinum oxides, and Engler and Wochler (*Z. anorg. Chem.*, xxix. p. 1) have definitely proved that a platinum peroxide exists in platinum black, which acts as an oxygen carrier, so that they class all platinum catalyses as "pseudo-catalytic"—that is, as brought about by intermediate reactions which go on much more quickly than the direct action. We may take it as probable that ultimately most, if not all, "catalytic" processes will be recognised as "pseudo-catalytic" in that sense.

Already before these publications, Haber and Grinberg (*Z. anorg. Chem.*, xviii. p. 39; *Z. physik. Chem.*, xxxiv. p. 515) and Bredig (*ibid.*, xxxi. pp. 294, 346, and *Anorg. Fern.*, 1901, p. 942, with his co-operators Müller von Berneck, Ikeda, and Ernst) had pointed out that in platinum catalyses the first phase is the formation of a platinum oxide (otherwise shown to probably exist by the experiments of Mond, Ramsay, and Shields, *Z. physik. Chem.*, xxv. p. 685), which is reduced in the second phase, *e.g.* by  $\text{H}_2\text{O}_2$ , with evolution of oxygen.

Brode (*Z. physik. Chem.*, xxxvii. p. 257) has, in the case

of molybdenum and tungsten compounds as oxygen carriers, shown the quantitative kinetic working of the intermediate reactions in catalysis.

We now pass on to the special processes going on when sulphur dioxide and oxygen are made to combine by contact-action. Here we enter upon the experimental field. We have quoted (p. 1288) Winkler's trials of 1875, in which he succeeded in recombining 78 per cent. of the mixture of  $\text{SO}_2$  and  $\text{O}$ , obtained by decomposing  $\text{H}_2\text{SO}_4$  by strong heat. No higher figures of yield are recorded anywhere else for Winkler's process in literature; although it was undoubtedly repeated hundreds of times on the small and also on the large scale, nothing was published about it till we come to the work of Knietsch. We do not therefore know what are the best results obtainable with that process, but even from theoretical considerations we may conclude that it could never lead up closely to a *complete* conversion of  $\text{SO}_2$  into  $\text{SO}_3$ . This is, for instance, pointed out by Sackur (*Z. Elektrochem.*, viii. p. 47). The assumption that 1 mol.  $\text{SO}_2$  could be converted into  $\text{SO}_3$  by a single atom of  $\text{O}$  is contrary to the law of the action of masses. Since the reaction  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  is reversible, that law leads to the equation:

$$\frac{(\text{SO}_2)^2 \times (\text{O}_2)}{(\text{SO}_3)^2} = k; \text{ hence } \frac{\text{SO}_3}{\text{SO}_2} = \sqrt{\frac{\text{O}_2}{k}},$$

which means that the yield of  $\text{SO}_3$  is all the larger, the greater the concentration of the oxygen.<sup>1</sup> The same author maintains that in theory dilution with nitrogen must influence the yield unfavourably, but in practice this does not matter, as the gases are not diluted with pure nitrogen, but with air, and thus the concentration of oxygen is increased at the same time, which alone is decisive for the yield.

E. J. Russell and Norman Smith (*J. Chem. Soc.*, 1900, lxxvii. p. 340) have made some interesting experiments on the combination of sulphur dioxide and oxygen. They found that even at the ordinary temperature certain metallic oxides

<sup>1</sup> According to Thalheim the correct form of the equation is:

$$\frac{(\text{SO}_2)^2}{(\text{SO}_2)^2 \times \text{O}_2} = k; \text{ hence } \frac{\text{SO}_3}{\text{SO}_2} = \sqrt{k(\text{O}_2)}.$$

action of  $\text{Fe}_2\text{O}_3$ , as due, firstly, to the successive reduction of this oxide by  $\text{SO}_2$  to  $\text{Fe}_3\text{O}_4$ , with formation of  $\text{SO}_3$ , and the re-oxidation of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  by free oxygen; secondly, to the simultaneous fixation of  $\text{SO}_2$  and O in the form of  $\text{Fe}_2(\text{SO}_4)_3$ , and the splitting up of this into  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$ .

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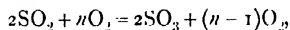
Brode (*Z. physik. Chem.*, xxxvii. p. 257) has, in the case



practical aspects of catalysis, containing no original matter (*J. Soc. Chem. Ind.*, 1902, p. 302).

We now come to the paper by Knietsch (*Berl. Ber.*, 1901, pp. 4093 *et seq.*), which is the most complete hitherto published on this subject. It is accompanied by a set of curves, reproduced in Fig. 487, which illustrate the progress of the reaction under various conditions. Let us first take a gas, containing 20 vol.  $\text{SO}_2$ , 10 vol.  $\text{O}_2$ , and 70 vol.  $\text{N}_2$ —that is, apart from nitrogen, a stoichiometrical mixture of sulphur dioxide and oxygen. Whatever be the temperature and the velocity of the current, we see from the curves S and S' that the maximum, which always occurs at  $430^\circ$ , is 77 to 78 per cent. with a current of 1000 c.c. per minute, or 90 to 91 per cent. with 500 c.c. per minute. Nor can a pure mixture of  $\text{SO}_2$  and O in Winkler's proportions, as shown in curve S'', reach a quantitative conversion into  $\text{SO}_3$ .

If, however, mixtures are employed in which either oxygen or sulphur dioxide is present in excess, it is possible by the action of masses of one of the constituents to displace the other constituent almost completely by converting it into  $\text{SO}_3$ . Therefore a process for manufacturing  $\text{SO}_3$  by contact-action will go on all the better, the more oxygen is present in proportion to sulphur dioxide, the nitrogen being quite indifferent. The formula of conversion ought therefore to be written:—



and  $n$  should not be less than 2.

Let us now take a technical pyrites-kiln gas, containing 7 per cent. (vol.)  $\text{SO}_2$ , 10 per cent.  $\text{O}_2$ , and 83 per cent.  $\text{N}_2$ , which corresponds to about  $2\text{SO}_2 : 3\text{O}_2$ . Even when passing it through an empty porcelain tube there is some formation of  $\text{SO}_3$ ; curve P shows the maximum to be 30 per cent. at  $600^\circ \text{C}$ .<sup>1</sup> We now fill the tube with platinised asbestos, containing 5 to 10 per cent. platinum, in such a manner that the first half of the tube remains empty and serves merely to heat the gases, the other half containing about 0.5 g. platinum mixed with the asbestos. Curve No. 1, referring to a velocity of 300 c.c. per minute, shows the first trace of  $\text{SO}_3$  a little over  $200^\circ$ , and a

<sup>1</sup> Cf. above, pp. 1282 and 1283, the attempts at forming  $\text{SO}_3$  by merely heating the roasting-gases in flues filled with pebbles, etc.

ISOTHERMOUS REACTION  $2\text{SO}_2 + 3\text{O}_2 \rightleftharpoons 2\text{SO}_3 + 2\text{O}_2 + 22600 \text{ CAL.}$

- Platinum contact  
 — Spectrometrical burner gas  
 S' — Pure isochrometrical mixture  
 F. — Pyrites cinders ( $\text{FeS}_2$ ,  $\text{CuO}$ ) as contact substance D.
- P. — Bits of porcelain as contact substance.  
 E. —  $\text{SO}_3$  with porcelain contact substance.  
 D. —  $\text{SO}_3$  in the empty porcelain tube.

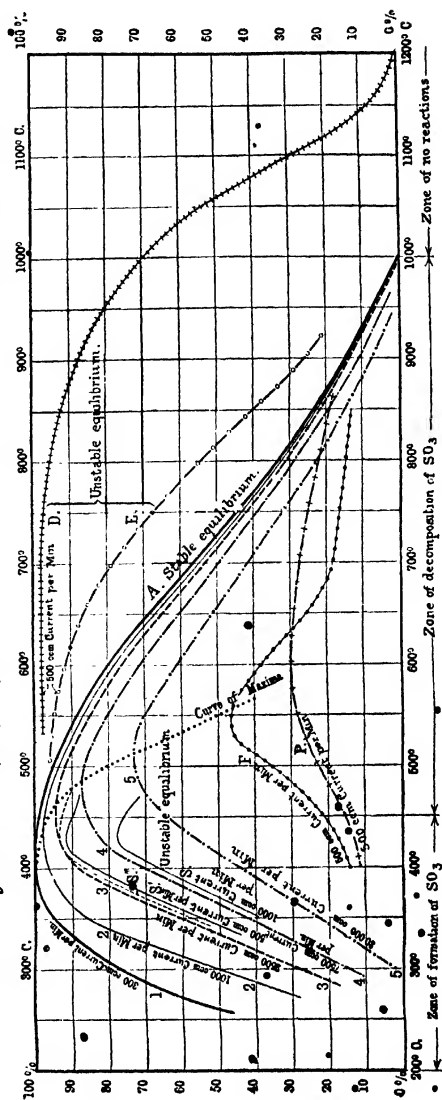


FIG. 487.

## 1308 MANUFACTURE OF FUMING OIL OF VITRIOL

rapid increase of the formation of  $\text{SO}_3$ , which is practically complete at  $380^\circ$  to  $400^\circ$ . From  $400^\circ$  to  $430^\circ$  the quantitative action is almost constant=98 to 99 per cent.; but then the curve descends, although more gently than it had risen, the  $\text{SO}_3$  being more and more dissociated into its components. At  $700^\circ$  to  $750^\circ$  only about 60 per cent. of the  $\text{SO}_2$  is converted into  $\text{SO}_3$ , at  $900^\circ$  to  $1000^\circ$  the curve reaches the zero-point.

If we repeat the experiments, changing only the quantity of contact-substance or, what comes to the same thing, increasing the strength of current, we obtain the curves No. 2 (1000 c.c. per minute), No. 3 (2500 c.c.), No. 4 (7500 c.c.), No. 5 (30,000 c.c.). These curves in their ascending branch run, for certain distances, almost parallel, but slightly diverging, which points to a common starting-point. But the descending branches all distinctly converge and ultimately all reach zero at temperatures between  $900^\circ$  and  $1000^\circ$ .

If we turn our attention to the highest points of the various curves, we observe that the maxima have a peculiar direction towards *higher* temperatures for *decreasing* quantities of platinum (or increase of velocity of the gases), and at the same time a strong decrease of the highest attainable degree of percentage conversion of  $\text{SO}_2$  into  $\text{SO}_3$ . If these maxima are joined by a curve, marked . . . . . in Fig. 487, we find its left-hand portion directed asymptotically towards the theoretical maximum of 100 per cent. conversion, the right-hand portion directed towards a point near  $600^\circ$ .

The close approach of the curves on the side of decomposition would lead to the assumption that the dissociation of sulphuric anhydride becomes, with the decrease of platinum, more and more independent of the contact-substance and also more and more a pure function of temperature. We may test this assumption by working without any platinum, having previously brought the gaseous mixture into the state of nearly complete conversion into  $\text{SO}_3$ . That experiment was made, but yielded a very surprising result, as shown by curve D. This curve is thereby shifted to the right hand by several hundred degrees, and begins to descend only at  $800^\circ$  to  $900^\circ$  C., without reaching zero even at  $1100^\circ$  to  $1200^\circ$ . This shows that *sulphuric anhydride, once formed, is very stable at high temperatures in the absence of contact-substances.* But this is an *unstable equilibrium*.

which is at once changed by the presence of any contact-substance and tends towards a *stable* equilibrium. Curve E shows this influence, consisting in a gradual approach of curve D to A, when repeating the experiment as at D, but with a tube filled with pieces of porcelain. We are thus reminded of the phenomena of superfusion and retardation of boiling, and at such temperatures porcelain and other substances prove to be similar catalysers to platinum. But it seems extraordinary that at such temperatures, viz., a vivid red-heat, such a strong retardation in reaching a stable equilibrium takes place.

Bodenstein (*Chem. Zeit.*, 1902, p. 1077) holds that the preceding observation of Knietzsch, according to which the porcelain contact does not form  $\text{SO}_3$  so easily as platinum contact, but does not destroy the formed  $\text{SO}_3$  in the same ratio, is a simple case of thermodynamics.

We have seen above that the reactions plotted in curves 1, 2, 3, 4 are dependent upon the duration of the contact of the gas with the contact-substance. This is made clearer by the curve Fig. 488, where on the X-axis the times of contact or, what comes to the same thing, the quantity of platinum is plotted, on the Y-axis the percentage proportion of  $\text{SO}_2$  transformed into  $\text{SO}_3$ . We perceive from this curve at once what time or what quantity of platinum is required for a certain percentage formation of  $\text{SO}_3$  for a definite temperature. We also perceive that the curves begin at zero and run asymptotically parallel to the X-axis, tending towards the maximum corresponding to the temperature. We also see that with the increase of temperature and the percentage increase of  $\text{SO}_3$  the curves get more and more bent, but more and more removed from a perfect transformation. Ultimately the velocity at the commencement is so great that at higher temperatures the beginning of the curves almost coincides with the Y-axis. Hence the first meeting of the roasting-gases with the contact-substance must lead to a violent reaction, and therefore to a strong heating of the first portions of the contact-substance, which, according to the kind of external coaling, may go up to a visible glowing.

We see further from the curves that at the formerly generally employed temperature of the contact-furnaces the reaction could not possibly be quantitative, and that it is only

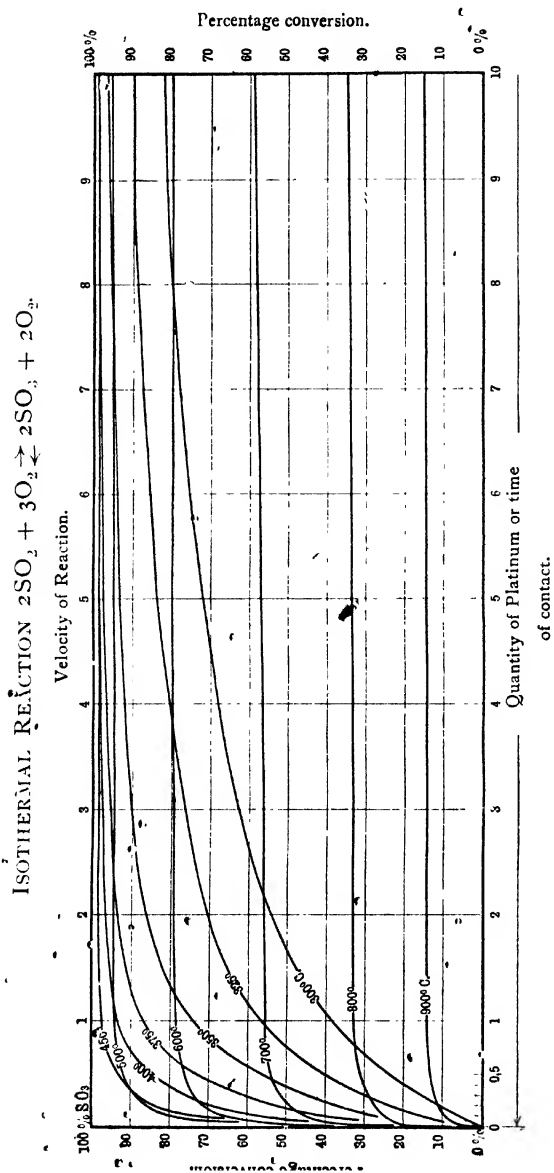


FIG. 488.

the sulphur trioxide itself which strongly retards the velocity of the reaction.

The most important result of Knietsch's experiments was that a line of *stable* equilibria exists which divides the range of temperature into two parts. The ranges below  $200^{\circ}$  and above  $900^{\circ}$  or  $1000^{\circ}$  may be called devoid of reaction in a technical sense; between  $200^{\circ}$  and  $450^{\circ}$  the reaction of formation prevails, above  $450^{\circ}$  the dissociation of  $\text{SO}_3$  comes into play very rapidly. •

From these facts important technical conclusions may be drawn. Although the limiting line A (Fig. 487) has been worked out only for a certain technical mixture of gases, we may safely assume that the different practically important cases will not have very much influence on the *position* of this stable equilibrium. This limiting-line must theoretically and practically be independent of the nature of the contact-substance; hence only those contact-substances will be able to produce a quantitative reaction in *one* operation which exhibit the maximum of activity below  $450^{\circ}$ . All contact-substances which exhibit their maximum activity only beyond that temperature (such as pyrites-cinders containing  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ , cf. curve F, p. 1307) will never be able to produce a quantitative conversion of  $\text{SO}_2$  into  $\text{SO}_3$ , whatever the length of time that may be employed. Hitherto only one substance has been found to fulfil the necessary conditions, viz., platinum, which cannot be replaced by any other member of the same group of metals with even approximately similar success.

The preceding conclusion of Knietsch has been hitherto justified by the fact that notoriously in those cases where ferric oxide, whether in the technically pure state or mixed with other oxides, is employed, the conversion never even approximately reaches 100 per cent., but only 60 to 66 per cent., and the end of the reaction is brought about by a second passage over platinum black. The theory of the contact-action of ferric oxide has been touched upon before (pp. 1301 *et seq.*). From the factories where it is actually employed no experiments have been published thereon, but an experimental investigation on that point has been made by myself, together with G. P. Mollitt, which will be subsequently mentioned. •

A further important paper has been published by Dr

Knietsch, in the *Transactions of the 5th Congress of Applied Chemistry*, i. pp. 614 *et seq.* (1904), in continuation of his paper of 1901, *suprà*, p. 1306. He had then proved that pure N shifts the equilibrium of the reaction downwards, but air or oxygen, by the action of masses, does so upwards. Hence the N is indifferent, but every contact-process for  $\text{SO}_3$  will go on all the better the more O there is in proportion to the  $\text{SO}_2$ .

It was important to ascertain how far the law of the action of masses in this case is of technical importance, and for this purpose a number of experiments have been made. To render these experiments reliable, numerous conditions have to be strictly adhered to, as explained by the author. A constant stream of gases, at constant pressure and constant temperature, was passed over a certain quantity of platinised asbestos during eight to ten hours. The composition of the gases was constantly, in equal distances of time, ascertained by titration with iodine solution, which yields very accurate results. The average constancy of the gaseous mixture was assured by taking them directly from the manufacturing apparatus. The constancy of the temperature of the electric furnace was obtained by means of an alternating current. The constancy of the catalytic force was secured by employing platinum asbestos, previously employed for the contact-process, for a fortnight. The strength of the current was constantly controlled. The results of the experiments are given in detail in the original; here we give only the final results.

(1) *Dilution with Nitrogen*.—A mixture of 66.67 per cent.  $\text{SO}_2$  with 33.33 per cent.  $\text{O}_2$  at  $430^\circ$  showed a yield of 94 per cent.  $\text{SO}_3$  after diluting with nitrogen (20 per cent.  $\text{SO}_2$ , 10 per cent.  $\text{O}$ , 70 per cent. N), the yield was 90.5 per cent.  $\text{SO}_3$  of the theoretical quantity. When diluting burner-gas with nitrogen (3.6 per cent.  $\text{SO}_2$ , 5.2  $\text{O}_2$ , 91.2  $\text{N}_2$ ) the conversion reached 98.24 per cent. In the original detailed calculations are given, showing that the nitrogen had no influence on the reaction.

(2) *Dilution with  $\text{CO}_2$* .—While pure burner-gas, at  $470^\circ$ , gave 96 per cent.  $\text{SO}_3$ , that gas diluted with an equal volume of  $\text{CO}_2$  gave 94.33 (calculated 94.7). This result is important, since in the manufacture of phthalic acid (for synthetic indigo)

very large quantities of gases, containing much  $\text{CO}_2$ , must be submitted to the contact-process.

(3) *Dilution with Aqueous Vapour*.—One vol. burner-gas with 13.5 or 26.7 vol. per cent.  $\text{H}_2\text{O}$ -at  $460^\circ$  gave 96.76 to 97.8 per cent. conversion. Here a slight diminution of the catalytic force of platinum takes place; but this can be neglected for practical purposes, since the admixture of so much aqueous vapour would anyhow yield sulphuric acid of insufficient strength.

(4) *Dilution with Air*.—(Equal volumes) at  $430^\circ$ ,  $560^\circ$ , and  $640^\circ$  gave results entirely corresponding with the theory.

(5) *Influence of Pressure*.—(a) 5.3 atm. at  $430^\circ$ , (b) 0.31 atm. at  $490^\circ$ , equally give results entirely foreseen by the theory.

The probably strict validity of the law of mass-action having been proved, some of the results calculated thereupon possess also practical interest. Thus it follows that the same technical effect is reached, whether the equilibrium be shifted by compression of the burner-gas, or by increasing the proportion of oxygen by adding pure oxygen to the gaseous mixture. A multiplication of the pressure in atmospheres is, in respect of the equilibrium to be obtained, equivalent to a multiplication of the oxygen percentage at the equilibrium under constant pressure. The following table shows this in figures:—

	Conversion increases		
	From	From	
Burner-gas of 1 atm.	Per cent. 60.0	Per cent. 80.0	Burner-gas with $1\text{O}_2$ " " $2\text{O}_2$ " " $3\text{O}_2$ " " $5\text{O}_2$ } at the equilibrium 1 atm.
" 2 " to	68.2	84.8	
" 3 "	72.3	87.2	
" 5 "	77.0	89.7	

This table shows that with a contact-substance which, e.g., has its most favourable action at  $600^\circ$  to  $700^\circ$ , but which at the ordinary pressure does not produce a yield of 60 per cent. (80 per cent.), neither an increase of pressure nor the addition of oxygen will allow of increasing the yield. The calculation of similar cases will, therefore, in future cause an abstention from useless experiments.



On the other hand, the formula of the law of mass-action tells nothing about the velocity of the reaction and the most favourable temperature—both of them most important practical factors. The general application of that law in the chemical industry is of long date. In Deacon's chlorine process, in the manufacture of ammonia soda, in the Hargreaves salt-cake process, in the processes for esterification and saponification, the best possible utilisation of a valuable reagent has been attained by employing another cheaper reagent. The novelty here is only the exact mathematical formulation of the law, which for this case has been reduced by Knietsch to the simple expression :

$$\frac{\text{SO}_3}{\text{SO}_2} = \frac{100\sqrt{\text{KO}_2}}{1 + \sqrt{\text{KO}_2}}$$

K denoting the concentration in volume per cent.

On the other hand, the sulphuric-acid contact-process would not have been developed more quickly than it has actually done, if these modern ideas had been uttered at an earlier stage; both because the results of modern theoretical chemistry were not known at that time, and because in practical work precisely those factors had to be avoided which are indicated as useful by theory, viz. application of pressure and removal of nitrogen from the roaster-gas. Practical men had to find ways of attaining theoretical yields without these costly means.

We shall find further contributions to the theory of platinum catalysis in the original communication of Dr Krauss, of Höchst, to be given later on.

Brode, in the paper mentioned in Chapter VII. p. 1010 (*Z. angew. Chem.*, 1902, p. 1081), quotes the views of Krauss, as shown in the British patents of 1901, with full approval. We shall in this place give merely a short extract from Brode's paper. The catalytic action of platinum in the reaction  $\text{SO}_2 + \text{O} = \text{SO}_3$  is technically applicable between  $400^\circ$  and  $500^\circ$ . But already at  $400^\circ$  the counter reaction sets in and is almost complete at  $1000^\circ$ . Although, therefore, a higher temperature would increase the velocity of the formation of  $\text{SO}_3$  (at  $500^\circ$  it is 200 times as strong as at  $400^\circ$ ), the equilibrium is shifted to the detriment of the product desired.

Practically it is impossible to work at the temperature at which the reaction is complete, because the velocity would be too small. In order to combine the highest velocity with a nearly quantitative yield, we must draw the consequences of the law of the action of masses; that is, we must either increase the concentration of the substances to be changed, or lower the concentration of the product to be obtained. The former cannot be done at will; the concentration of the  $\text{SO}_2$  is given, and merely the oxygen may be concentrated by employing more air, as the Mannheimer Verein has prescribed in their respective patent (see below). It is, however, not feasible to go too far in this direction, both from practical and theoretical grounds, at least not when working with atmospheric air, where any raising of the concentration of oxygen beyond 17 per cent. (with 3 per cent.  $\text{SO}_2$  and 80 per cent. N) would have but a very slight effect, the yield being proportional to the square root of the concentration of oxygen. It is therefore proper to proceed in the other direction, that is, to lower the concentration of the product obtained,  $\text{SO}_3$ , by taking it away by continuous or successive absorption. In this case the equilibrium is constantly disturbed, the reaction recommences, and ultimately all  $\text{SO}_2$  is changed into  $\text{SO}_3$ , even under unfavourable conditions of equilibrium. Hence we need not work at the optimum temperature of  $450^\circ$ , but, if proceeding as indicated, we may go considerably beyond that, and we shall then do far more work in a given apparatus in the same time, and we may also then employ catalysers which act only at higher temperatures. The first action will be best performed at high temperatures and corresponding velocities, and when the equilibrium has been reached, lower temperatures will be applied in order to perfect the yield.

From a paper by G. Lunge and G. P. Pollitt, in *J. Soc. Chem. Ind.*, 1903, p. 79, on the formation of sulphur trioxide by the action of ferric oxide, I quote only the conclusions:—

(1) The degree of change of  $\text{SO}_2 + \text{O}$  to  $\text{SO}_3$  is not sensibly affected by changes in dilution from 2 to 12 per cent. of  $\text{SO}_2$  by volume. A still greater dilution would probably act equally well (*vide* Sackur's theoretical observations, *supra*, p. 1304). Above 12 per cent. the percentage change is not only lowered, apparently in consequence of the too small excess of oxygen

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but also the contact-action of the oxide is lessened for more dilute mixtures.

(2) The mixture of gases to be changed into  $\text{SO}_3$  must be as dry as can be obtained by a thorough treatment with sulphuric acid. The neglect of this precaution not only causes the contact-action to be at once much lessened, but, in addition to this, the contact-mass has to be treated for a long time with the dry mixture before it recovers from the "poisoning" action of the moisture.

(3) Exactly the same results are obtained as by treating with moist gases when oxide of iron (pure or containing copper) which has been exposed to the air, and has therefore absorbed some moisture, is used. Only after long treatment with the gases at red-heat (lasting thirty hours or more) does the oxide of iron reach its maximum contact-action, which, however, immediately sinks again if the oxide after cooling is even during a short time exposed to the air.

(4) An improvement of the contact-action by methods of treatment having for their object the loosening of the surface of the oxide of iron was not achieved. Oxides obtained by heating ferri- or ferrosulphate gave a much lower contact-action than that obtained with an oxide prepared by igniting precipitated hydroxide, or in the form of pyrites-cinders. Doubtless the physical state of the oxide has a great influence on its catalytic action, but the authors did not succeed in clearing up this point.

(5) An addition of cupric oxide to the iron oxide (using the cinders from pyrites containing copper) is favourable to the formation of  $\text{SO}_3$ .

(6) Arsenious acid is completely taken up and retained by oxide of iron at a high temperature. (The best temperature seems to be about  $700^\circ \text{C}$ .) The oxide of iron can be thus charged with arsenic up to considerable quantities. An oxide thus charged, if it contains  $2\frac{3}{4}$  per cent. of arsenic (reckoned as As), shows a very considerably increased contact-action (over 60 per cent.) in comparison with the pure oxide.

(7) Oxide of iron containing copper also shows a distinct increase of contact-action on being charged with arsenic.

(8) The best temperature for the catalytic action of ferric oxide in the formation of  $\text{SO}_3$  lies between  $600^\circ$  to  $620^\circ \text{C}$ .

Below  $600^{\circ}$  the action is very slight; above  $620^{\circ}$  the catalytic action falls quickly to a certain point and remains constant till  $750^{\circ}$ , when it again begins to fall. The fall on raising the temperature must be attributed to the fact that the system  $\text{SO}_2 + \text{O} \rightleftharpoons \text{SO}_3$  tends to alter its condition of equilibrium, in the direction from right to left, on raising the temperature. The fact that there is no appreciable change between the temperatures of  $635^{\circ}$  and  $750^{\circ}$  can perhaps be best explained by assuming that two kinds of intermediate reactions come into play, viz.: first, the formation and decomposition of ferrisulphate; and, secondly, the alternating reduction of  $\text{Fe}_2\text{O}_3$  and oxidation of the  $\text{Fe}_3\text{O}_4$  so formed, and that these reactions have different optima of temperature.

A continuation of that work is contained in the paper of Lunge and Reinhardt (*Z. angew. Chem.*, 1904, pp. 1041 to 1051). Their results are summed up as follows:—(1) The catalytic combination of dry sulphur dioxide and atmospheric oxygen under the conditions adhered to in this entire series of experiments is first perceived a little above  $400^{\circ}$ , and attains its maximum of about 70 per cent. at  $625^{\circ}$ , above which temperature it goes down again. (2) These results are not sensibly modified by the circumstance whether the gases are dried merely by concentrated sulphuric acid, or over and above this by phosphorous pentoxide. (3) Ferric oxide in the shape of pyrites residues, loaded with arsenious acid, in the best case yielded about the same degrees of conversion as pure  $\text{Fe}_2\text{O}_3$ , about the same as attained by Lunge and Pollitt with ferric oxide charged with arsenic, but essentially higher than those obtained with pure ferric oxide by Lunge and Pollitt. (4) The same degree of conversion, about 70 per cent., is attained by ferric arsenate, prepared in the wet way, and at the same temperature ( $625^{\circ}$ ). Decidedly less active is ferric arsenic prepared in the wet way, but apparently not constituting a homogeneous compound. (5) Arsenic pentoxide free from iron possesses strong catalytic powers for the reaction  $\text{SO}_2 + \text{O} = \text{SO}_3$ , the maximum being at about  $675^{\circ}$ . (6) The admixture of a little cupric sulphate or oxide to the ferric oxide has no influence; but larger quantities of  $\text{CuO}$  decidedly diminish the catalytic power, and pure cupric oxide is still less active. (7) Jena glass and glazed or unglazed Berlin porcelain

have a very slight catalytic power for the reaction here treated; it becomes sensible only at  $700^{\circ}$ , and is hardly amenable to quantitative determination. On the other hand, pure silicium dioxide, both in the state of rock-crystal and of amorphous quartz glass, possesses a distinct catalytic action on the combination of  $\text{SO}_2$  with  $\text{O}$  to  $\text{SO}_3$ , which attains its maximum (up to 10 per cent.) at  $700^{\circ}$ .

As a continuation of these researches, Berl (*Z. angew. Chem.*, 1905, pp. 254 *et seq.*; more explicitly *Z. anorg. Chem.*, vol. xlv, pp. 267 to 299) in my laboratory examined the velocity of the reaction  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ , with arsenic pentoxide as catalyser, since this compound has proved to be a valuable agent in that respect, either by itself or in combination with ferric oxide, while in the catalysis by platinum it acts as a strong contact-poison. The investigation was based on measuring the pressures of the gases at constant volumes, by means of a specially constructed apparatus. On employing a stoichiometrical mixture of  $2\text{SO}_2 + \text{O}_2$ , a perfect reaction reduces the pressure to two-thirds. The contractions taking place during an experiment in certain intervals of time show the progress of the reaction. The catalyser was employed in some cases in the shape of a tubular layer of  $\text{As}_2\text{O}_5$  on a glass tube; mostly, however, in a granular, very porous shape. The results obtained were as follows. The observations of Lunge and Reinhardt, according to which arsenic pentoxide is a catalyser, comparable to ferric oxide, vanadium pentoxide, etc., was confirmed. Its catalytic power at first decreases and then acquires a constant value. The best action took place with gases, dried by concentrated sulphuric acid; if there is any moisture present, the catalytic action strongly decreases, but, on the other hand, more intense drying, as obtained by phosphorous pentoxide, appears to be also injurious to some extent. The temperature-coefficient of the reaction between  $295^{\circ}$  and  $340^{\circ}$  is  $= 1.21$ , between  $340^{\circ}$  to  $380^{\circ} = 1.19$  for each  $10^{\circ}$  increase of temperature; hence the reaction must be considered as a reaction of diffusion, since for these a temperature-coefficient of 1.1 to 1.4 has been ascertained, whereas for purely chemical reactions the coefficient is 2.0 to 3.0, and upwards, for each  $10^{\circ}$  increase of temperature. The reaction is hastened, both by increasing the concentration of  $\text{SO}_2$  and that of  $\text{O}_2$ , but more so with the

former. The relative velocities, referred to per cent. of  $\text{SO}_3$  formed, are almost equal.  $\text{SO}_3$  has a strongly retarding action on the velocity of the reaction, explicable by the formation of a thin layer of it forming on the catalyser. An admixture of indifferent gases, as  $\text{N}_2$  and  $\text{CO}_2$ , influences the velocity of reaction in the direction following from the results of Nernst (*Z. physik. Chem.*, xlvii. p. 54) and Brunner (*ibid.* p. 56).

I have been favoured by Dr Brode, of Karlsruhe, with the following remarks on the maximum yield theoretically obtainable in the manufacture of  $\text{SO}_3$  by the contact method. From the graphic representation given by Knietsch (p. 1307), it appears that he had obtained from technical burner-gases the equilibrium  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  at temperatures over  $450^\circ \text{C.}$ , since the yield did not change after some time or when employing more contact-substance. At lower temperatures the yields were still gradually increasing, and hence the equilibrium was not yet reached. As Knietsch worked with gases containing 7 per cent.  $\text{SO}_2$ , 10  $\text{O}_2$ , and 83  $\text{N}_2$  by volume, we can calculate the equilibrium constant  $K$  for temperatures upwards of  $450^\circ$  by the formula :

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

and we thus arrive at the following table, in which column I shows the temperatures ; II. the yields obtained by Knietsch (as read off from the curves) ; III. the proportion  $\text{SO}_3 : \text{SO}_2$  calculated therefrom ; IV., V., VI. the concentrations of the single gases at equilibrium, expressed in per cent. by volume ; VII. the constant, expressed in the same way. •

I.	II.	III.	IV.	V.	VI.	VII.
°C.	Yield 100 $\text{SO}_2$ $\text{SO}_2 + \text{SO}_3$	$\frac{[\text{SO}_3]}{[\text{SO}_2]}$	SO <sub>2</sub> SO <sub>3</sub> O <sub>2</sub> Per cent. vol.			Constant K.
	Per cent.					
450	98	49.00	6.86	0.14	6.6	364.0
500	95	19.00	6.65	0.35	6.7	54.0
600	80	4.00	5.60	1.40	7.2	2.2
700	59	1.10	4.13	2.87	7.9	0.25
800	35	0.54	2.45	4.55	8.8	0.033
900	15	0.18	1.05	5.95	9.5	0.0034

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The constant now allows us to calculate the maximum yields obtainable at given temperatures and concentrations of oxygen for the case that the equilibrium is actually obtained, and independently of the contact-substance (according to van't Hoff, *Vorles. chem. Dyn.*, p. 21). For each temperature the relation is:

$$\sqrt{K[O]_2} = \frac{[SO_3]}{[SO_2]}$$

and the percentage yield:

$$\frac{100[SO_3]}{[SO_3] + [SO_2]} = \frac{100\sqrt{K[O_2]}}{1 + \sqrt{K[O_2]}}$$

In the subjoined table, column I. shows the results obtained experimentally by Knietsch with technical burner-gases containing 7 vol. per cent.  $SO_2$ , 10  $O_2$ , 83  $N_2$ ; II. the yields theoretically obtainable by the process employing great excess of air, assuming the concentration of oxygen at equilibrium = 16 vol. per cent.  $O_2$ ; III. the yields obtainable by burning sulphur in pure oxygen, the gases showing 7 vol. per cent.  $SO_2$  and 93  $O_2$ , and the oxygen concentration = 90 per cent. at equilibrium.

Temp. °C.	I.		II.		III.	
	Technical burner-gas.		Burner-gas with excess of air.		Burning S with pure oxygen.	
	$\frac{SO_2}{SO_2}$	Yield per cent.	$\frac{SO_2}{SO_2}$	Yield per cent.	$\frac{SO_2}{SO_2}$	Yield per cent.
450	48.0	98	76.0	98.7	181.0	99.5
500	18.5	95	29.3	96.7	70.0	98.6
600	4.0	80	5.8	86.0	14.0	93.0
700	1.4	59	2.0	67.0	4.7	81.0
800	0.54	35	0.73	42.0	1.7	62.0
900	0.18	15	0.23	19.0	0.55	36.0

Keppeler (*Z. anorg. Chem.*, 1902, p. 809) has made some interesting observations on the conditions to be fulfilled by every contact-substance. Apart from the property of forming two grades of oxidation, of which the higher is reduced by  $SO_2$  at the same time as the lower is oxidised by O (*cf.* p. 1303 showing this property even in the case of platinum, according

to Engler and Woehler), those substances which form sulphates, like ferric oxide, must be considered in another respect as well. On heating sulphates they begin to give off molecules of  $\text{SO}_3$  in a proportion increasing with the temperature; and for each temperature they continue to do this until the vapour of  $\text{SO}_3$  in the space above the sulphate has a tension equal to that with which the  $\text{SO}_3$  is split off from the oxide. If that equilibrium is disturbed by the change of atmosphere, the sulphate again splits off  $\text{SO}_3$ , and this goes on until only oxide remains. Hence it is unnecessary to work at a temperature at which the dissociation of the sulphate is complete, that is, until the tension is equal to that of the atmosphere. It is only necessary that the partial pressure of the vapour of  $\text{SO}_3$  should be less than the tension of dissociation of the sulphate at that temperature. With the dilution of the burner-gases the temperature is lowered at which the contact-substance is active. If, for instance, the burner-gas can furnish 8 per cent.  $\text{SO}_3$ , a temperature suffices at which the  $\text{SO}_3$  vapour split off by the sulphate have a tension of 0.08 atm. At  $400^\circ$  the  $\text{SO}_3$  tension of ferric sulphate is not sensible; it becomes so at  $500^\circ$ , and probably it is not necessary to exceed that temperature largely if very dilute gas (2 to 3 per cent.  $\text{SO}_3$ ) is employed, because then the temperature required for the formation of sulphate is much lower: the excess of oxygen is useful through the action of the law of masses, and the heat of reaction, being applied to a greater mass, does not produce a harmful rise of temperature.

Keppeler's further work on the catalytic function of ferric oxide in the formation of  $\text{SO}_3$  is found in *Z. angew. Chem.*, 1908, pp. 532 *et seq.*, and pp. 557 *et seq.*, and *Z. physik. Chem.*, 1908, vol. lxii, pp. 89 to 118. He found that it is a decided advantage to effect the catalytic action in two stages, of which the first may be performed by platinum even at a higher temperature, the second at  $450^\circ$  to  $500^\circ$ ; the yield is almost quantitative. He measured the dissociation tension of ferric sulphate in a current of nitrogen, as well as in a current of oxygen; the latter is much less than the former. Also the best conditions for obtaining  $\text{SO}_3$  from burner-gases consisting of 7 per cent.  $\text{SO}_2$ , 10 per cent. O and 83 per cent. N; he found the optimum at  $665^\circ$ , and he compares his results both with those of other



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laboratory investigations and with those obtained in large scale work (as far as the latter can be learned). Concerning the essence of the ferric oxide catalysis, he considers it very probable that it takes place through a condensation of  $\text{SO}_2$  on the surface of the ferric oxide (by "adsorption"). The arsenic trioxide of the burner-gases is retained in the ferric oxide in the shape of pentoxide. More  $\text{SO}_3$  is produced than the ferric oxide could combine with, which refutes the assumption that the catalytic process is due to the temporary formation of ferric sulphate. Koppeler's paper is criticised by Wöhler, Plüddemann and Wöhler (see p. 1325).

Bodländer and Koppen (*Z. Elektrochem.*, 1903, ix. pp. 559, 698, 787) have worked on the speed of the formation of  $\text{SO}_3$  by the contact-process. Since the temperature at which that formation takes place with a technically available speed is near that at which a sensible dissociation of the  $\text{SO}_3$  sets in, the technical process must be carried on at a temperature at which the velocity of formation is as large as possible, the dissociation being as small as possible. The velocity of formation under various conditions, in the presence of platinum-wire net as a catalyser, was measured by the diminution of pressure shown by the gaseous mixture at constant volume and constant temperature, according to the equation:  $\text{SO}_2 + \text{O} = \text{SO}_3$ . If to the stoichiometrical mixture of  $\text{SO}_2$  and O varying quantities of N are added, the velocity of the formation of  $\text{SO}_3$  is dependent on the initial partial pressure of the gases, the degree of dilution with N. The presence of  $\text{SO}_3$  directly retards the reaction, apart from the dilution; excess of O and  $\text{SO}_2$  increases it qualitatively, and, approximately, also quantitatively;  $\text{SO}_2$  does so more than the oxygen, as foreseen by the theory. The speed of reaction increases with a rise of temperature (1.42 times for each  $10^\circ$ ), but depresses the maximum yield of  $\text{SO}_3$ . Excess of air shifts the equilibrium in favour of the formation of  $\text{SO}_3$ , and also increases its speed; hence good yields may be obtained also at higher temperatures by greater excess of air, as is done in actual practice. Bodländer has also made a publication on that subject at the Fifth International Congress for Applied Chemistry, in Berlin, 1904 (*Verhandlungen*, iv. p. 624).

Küster (*Z. anorg. Chem.*, 1904, xlii. pp. 453 to 469) made a

series of experiments with various contact-substances, for which he constructed special apparatus such as a gas-holder, in which the gases come into contact only with mercury, so that no  $\text{SO}_2$ , etc., is absorbed by water, and a special heating-oven for the contact-tube. From the results he draws the following conclusions: (1) Platinum, vanadium pentoxide, and ferric oxide yield, for equal temperatures, the same equilibria for  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_3$ . (2) Of these three catalysers, platinum is by far the most efficient, and the only one which permits to attain the equilibria within technically useful times. (3) Water very strongly influences the catalytic power of ferric oxide and vanadium pentoxide, so that there exists an optimum of desiccation for both catalysers. This optimum is defined by the degree of desiccation, attained by ordinary commercial concentrated sulphuric acid. (4) Ferric oxide as a catalyser is very sensitive to mechanical and chemical influences, and is especially more and more poisoned by increasing quantities of arsenic. But the efficiency of vanadium pentoxide is permanent for an apparently unlimited time.

Another investigation of that subject has been made by Bodenstein and Pohl (*Z. Elektrochem.*, 1905, pp. 373 to 384). They establish the fact that the equilibrium of the catalytic formation of  $\text{SO}_3$  signally obeys the demands of the law of mass-action and of thermodynamics, and they state that the practical results obtained by Lunge and Reinhardt (*Z. angew. Chem.*, 1904, p. 1041) agree with this, but not the results of Bodländer and Köppen, nor those of Küster (see *supra*). The following tables calculated by them from their investigation give a good idea of the bearings of their investigation:—

(1) *Conversion of a Stoichiometric Mixture of  $\text{SO}_2$  and  $\text{O}_2$  into  $\text{SO}_3$  at various temperatures, when diluted with Nitrogen.*

No.	Amount of $\text{N}_2$ added.	$\text{SO}_2$ .	$\text{O}_2$ .	400°.	500°.	600°.	700°.	800°.	900°.
1	...	66.67	33.33	98.1	91.3	76.3	71.5	30.1	16.0
2	79.00	14.00	7.00	96.3	84.7	62.2	35.2	18.3	8.2
3	84.85	10.10	5.05	95.7	83.2	59.1	31.9	15.0	7.0
4	89.50	7.00	3.50	95.2	81.2	55.5	28.5	12.9	6.0
5	97.00	2.00	1.00	92.7	73.2	43.0	18.4	7.5	3.3

<sup>1</sup> Gas produced by burning sulphur in air.

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(2) *Sulphur Dioxide and Oxygen without Nitrogen.*

No.	N <sub>2</sub> .	SO <sub>2</sub> .	O <sub>2</sub> .	400°.	500°.	600°.	700°.	800°.	900°.
1	...	66.67	33.33	98.1	91.3	76.3	51.5	30.1	16.0
6	...	33.33	66.67	99.7	97.3	88.5	66.6	40.4	22.0
7	...	14.00	86.00	99.8	97.9	90.3	69.8	43.9	24.4
8	...	7.00	93.00	99.8	98.1	90.5	70.7	44.9	25.3
9	...	2.00	98.00	99.8	98.2	90.8	71.2	45.5	25.6

(3) *Burner-gas diluted with Air.*

No.	Air per cent.	N <sub>2</sub> .	SO <sub>2</sub> .	O <sub>2</sub> .	400°.	500°.	600°.	700°.	800°.	900°.
3	...	84.85	10.10	5.00	96.2	83.2	59.1	31.9	15.0	7.0
10	1.444	83.00	7.00	10.00	99.3	93.4	73.3	42.5	20.5	9.8
11	2.194	81.40	4.00	14.60	99.4	94.9	78.3	48.1	24.2	11.7
12	3.944	80.00	2.00	18.00	99.5	95.6	80.5	51.3	26.3	12.9

*Vide* also Bodenstein and Finck, *Z. physik. Chem.*, 1x. (1907), pp. 1 to 45.

Lucas (*Z. Elektrochem.*, 1905, p. 457) made an investigation on the SO<sub>3</sub> contact-process by manometrical methods. He found that the yield with a mixture of SO<sub>2</sub> and O<sub>2</sub> according to stoichiometrical proportions is better than with the "ideal" burner-gas (11.69 per cent. SO<sub>2</sub>, 5.85 per cent. O<sub>2</sub>, 82.46 per cent. N). The addition of a little air to the latter at once increases the yield, but lessens the velocity of reaction.

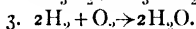
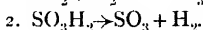
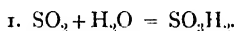
An important paper on the subject in question is that of Lothar Wöhler, Foss and Plüddemann, in *Berl. Ber.*, 1906, pp. 3538 *et seq.* They state that sulphur trioxide above 450° begins to split up (Knietzsch, *Ber.*, 1901, p. 4099; *suprà*, p. 1306); therefore the best catalysis must take place below 450°. Platinum shows its maximum of catalytic power, according to Knietzsch, at 400°, and is therefore in respect of yield the best catalyser for this purpose. The cause of its catalytic power is not yet cleared up. Engler and Wöhler (*Z. anorg. Chem.*, 1901, p. 1) considered it probable that the hypothetical platinum peroxide is formed as an intermediate product, but Wöhler later on (*Z. Elektrochem.*, 1905, p. 844) showed that this assumption is unnecessary, since the ordinary monoxide, PtO, already possesses the required strong oxidising power, and the catalytic decom-

position of  $\text{H}_2\text{SO}_2$  is produced far more vividly by platinum black than by platinum oxides.  $\text{PtO}$  is reduced by  $\text{SO}_2$  already at  $130^\circ$ , more vividly at  $200^\circ$ , and very fast at  $400^\circ$ . Experiments showed that, under identical conditions of temperature and velocity of the gaseous current,  $\text{PtO}$  at first shows only one-fifth of the action of metallic Pt, but later on the action of  $\text{PtO}$  increased up to that of Pt, and it was proved that this happened in the same proportion as the  $\text{PtO}$  was reduced by the contact-mixture to metallic Pt. Palladium behaves quite in the same way. The maximum contact yield when employing platinum is at  $400^\circ$ , for palladium it is at  $700^\circ$ , and iridium is midways between them. The formation of an exothermic oxide of the platinum group as active intermediate product of the contact-process is excluded, but an endothermic oxide may have that function. There are some indications for this, but the matter requires further investigation. We must refer to the original for the description of the experiments made on the catalytic action of Pt,  $\text{PtO}$ , and  $\text{PtO}_2$ , of Pd and  $\text{PdO}$ , on the action of Pd in contact-mixtures at  $808^\circ$ , and the comparison of the catalytic action of metallic Pt, Pd, and Ir.

A continuation of this research is the paper of L. Wöhler, Plüddemann and P. Wöhler, in *Z. physik. Chem.*, 1908, lxii. pp. 641 to 677. A comparison of the contact-action of  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ , cupric and cuprous chromite,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and the oxides of Th, Ce, and Ti, showed that the curves expressing the ratio of actual to theoretical yield, for equilibrium in relation to the temperature, all pursue a similar course, rising with the temperature, without showing a maximum. The sintering of the surface of the contact-substance during the heating was found to exert a very great effect on its action, and certain apparent maxima were found to be really due to this cause. The influence of the surface was found not to be proportional to the size of the particles. In the case of differently prepared or treated samples of the same substance, their adsorptive powers were found to be proportional to the efficiencies of their contact-action, but this relation does not exist when different substances are compared. The variation of adsorption with concentration depends upon the adsorbing substance; the exponent of adsorption varies between Q and K. The

action of the contact-substances in the sulphuric-acid process can be explained by the supposition of the intermediate formation of a solid solution of the gas components, whether it be of gas or of a solid chemical compound.

An entirely new theory of the catalytic conversion of  $\text{SO}_2$  into  $\text{SO}_3$  by means of platinum has been proposed by H. Wieland (*Berl. Ber.*, 1912, pp. 685 *et seq.*), on the strength of observations made on the action of damp  $\text{SO}_2$  on palladium black. He rejects the ordinary assumption, according to which platinum causes this combination of  $\text{SO}_2$  with atmospheric O to  $\text{SO}_3$ . It has been established long ago that *absolutely dry* gases are not catalytically combined to  $\text{SO}_3$ ; cf. *suprà*, p. 1305, the investigations of Russell and Smith, my own remarks, *suprà*, p. 1305, founded on the investigation made by myself with Pollitt in 1902, according to which a trace of water, such as remains after drying the gases with concentrated sulphuric acid, is necessary for the catalytic combination of  $\text{SO}_2 + \text{O}$ , whereas larger quantities of moisture act as a contact-poison, also the results of Berl, p. 1318, and Küster's similar conclusions, *suprà*, p. 1323. Wieland consequently explains the contact-process not essentially as an oxidising reaction, but as an abstraction of hydrogen, according to the following equations :



The part played by the oxygen, according to this theory, consists in immediately burning the hydrogen formed by No. 2, and the water formed thereby is constantly reintroduced into No. 1.

#### PRESENT STATE OF THE MANUFACTURE OF SULPHURIC ANHYDRIDE AND SULPHURIC ACID BY THE CONTACT-PROCESS.

This process is carried out in practice in a considerable number of modifications. About some of these nothing whatever is known outside the circle of those who work them, and concerning these I can naturally say nothing in this place. To this number belong the processes used by Messrs Chapman,

Messel, & Co., at Silvertown, by the United Alkali Company and by the Tentelw Chemical Works at St Petersburg [cf. a description of their apparatus in the B. P. 11969 of 26th May 1902, *J. Soc. Chem. Ind.*, 1903, p. 695].

Only six different processes are better known, partly by the patent specifications and partly by communications from the owners, most of which have appeared for the first time in this book. We may divide them into two classes:—

A. Processes by which the conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is rendered practically complete by contact-action (Badische, Höchst, Grillo, Mannheim).

B. Processes which supplement the contact-process by ordinary lead chambers for working up the residual gases (Freiberg, Rabe).

#### I. *The Process of the Badische Anilin- und Sodafabrik at Ludwigshafen.*

This process has been worked out by Dr Knietsch, who has described its rise and present state in a lecture delivered before the German Chemical Society on 19th October 1901, which has been published in *Berl. Ber.*, 1901, pp. 4078 *et seq.*

The whole of the matter contained in that lecture, as far as it refers to the subject in question, is given in the following description, which is, however, largely amplified by extracts from the patent specifications, and by a direct communication made to me by the Badische Anilin- und Sodafabrik.

When Knietsch approached the problem of completely converting pyrites-kiln gases into sulphuric acid by contact-action, this seemed to promise no success according to all that was known at that time in practice and theory. He was induced, in spite of this, to consider success possible principally from theoretical considerations.

We know that the gases issuing from the ordinary lead chambers still contain 6 per cent. oxygen. The same excess of oxygen must necessarily be present in every burner-gas submitted to the contact-process, and there was no apparent reason why the reaction should not go on quantitatively with such an excess of oxygen. This question was tested by experi-

ments with pure sulphur dioxide diluted with much air, and it was found that the reaction under certain conditions stopped quite short only of quantitative conversion. It was found that dilution with air to any extent had next to no influence on the conversion of  $\text{SO}_2$  into  $\text{SO}_3$ , nay, even that this conversion was promoted by diluting the  $\text{SO}_2$  with more air, and thus increasing the proportion of oxygen in comparison with dioxide. From this followed the fact that the view held up to that time, according to which diluting gases had an injurious effect on the contact-process, had to be critically examined.

The experiments were now extended to real burner-gases, taken from the pyrites-kilns and conducted to the laboratory through a long lead tube, acting like a flue-dust chamber in removing cinders, flue-dust, etc. The gases were also washed by several bottles charged with sulphuric acid. The results were almost as complete as those obtained with artificial mixtures of gases, and no falling off in the quantitative action was observed, although the experiments with the same contact-mass lasted several days.

This seemed to justify the hope that sulphuric acid might be almost quantitatively made in this way from burner-gases, and the experiments were repeated on the large scale; but it was soon found that the action of the contact-substance did not hold out during a prolonged use and ultimately it entirely failed. This result was not improved by cooling the gases in long flues and repeatedly washing them with sulphuric acid, nor by filtering them through dry coke and asbestos filters so that they might be regarded as pure as could be technically attained. So far, the process had failed on the large scale. But on making further laboratory experiments on the causes of the slow, but seemingly inevitable, retrogression of the contact-action it was found that some substances interfere with the catalytic action of platinum even when present in extremely small quantities. These are arsenic and mercury, also phosphorus, but later on the injurious effect of the latter was found to be caused by its contamination with arsenic. Other substances, such as antimony, bismuth, lead, iron, zinc, etc., are injurious only so far as they mechanically envelop and stop up the contact-mass, if introduced in large quantities. The injurious effect of arsenic is so great that 1 or 2 per cent. of the

weight of platinum suffices for depriving this entirely of its activity.<sup>1</sup>

The question now arose, whether those "contact-poisons," as they may be styled, are present in burner-gases after all the purifying operations above described, and it was found that indeed the whitish mist of sulphuric acid, which could not be precipitated, contained arsenic. Thus the want of success was partially cleared up, but no remedy was known, since up to that time the *complete* precipitation of these white mists was considered technically impossible by the most competent experts (*cf.* Schnabel's *Hüttenkunde*, 1890, p. 500). Still, the task was again taken in hand to accomplish a complete removal of *all* impurities, so as to leave a mixture of absolutely pure sulphur dioxide, oxygen, and nitrogen. An enormous amount of time, trouble, expense, and patience was required for attaining that object, first in the laboratory, and then on the large scale. The difficulty was principally caused by the continuous struggle with an *invisible* foe, and the fact that each mistake was attended by a lasting diminution of the yield of the whole plant. The result of the whole work is embodied in the patents cited below, which show that the burner-gases can indeed be completely freed from all impurities, if, after proper treatment and cooling, they are subjected to a prolonged systematic intimate contact with water or sulphuric acid, carried on until an optical and chemical examination proves their perfect purity. It is indifferent for the result in which way that intimate contact with the purifying liquids is attained, whether by intense washing, or wet filtration, or a combination of both. Only a few of the difficulties will be mentioned which occurred during the introduction of the purifying process into practical work.

It was found that the gases should be *slowly* cooled, in which case the sulphuric-acid mists are much more easily precipitated than when cooling rapidly (say, by bringing them into contact with much water)—a phenomenon which may be caused by different states of the sulphuric anhydride (p. 277),

<sup>1</sup> Winteler (*Z. angew. Chem.*, 1905, p. 1655) claimed for Clemens Winkler the merit of discovering the deleterious effect of arsenic in the platinum contact-process. The Badische Company (*ibid.*, p. 1902) energetically contradict him and vindicate that discovery for Knietisch.



but still awaits its proper explanation (*cf.* also p. 1284). The cooling required long *iron* conduits cooled by air. So far as was then known, the iron could not have any injurious effect, for acid with more than 90 per cent.  $\text{H}_2\text{SO}_4$ , such as must be formed when dry pyrites is employed, was not expected to act upon iron, or to yield at most  $\text{SO}_2$ , which could do no harm. But although the burner-gases had been completely purified, and even passed through wet filter-presses; and the optical test (at that time regarded as sufficient) betrayed no contamination, yet the contact-mass was slowly, but invariably, changed after weeks or months. After a long series of investigations, and only after the presence of arsenic, undiscoverable in the gases, had been proved in the platinum asbestos after having lost its activity, the assumption gained ground that the disturbance might arise from an attack of the small quantity of sulphuric acid condensing in the iron cooling-pipes, and that this must proceed from the formation of a gas containing arsenic, presumably arseniuretted hydrogen. Precautions were now taken that the condensing acid should not come into contact with iron, and from this moment the contact-furnaces retained their activity without any change. Consequently, contrary to the general view up to that time, the action of concentrated sulphuric acid on iron must have produced some hydrogen, for only in this way arseniuretted hydrogen could have been formed.

Another very enigmatical and protracted disturbance arose through the formation of mists in the pyrites-kilns, found after lengthy investigation to consist of very slight quantities of unburnt sulphur, which is just as difficult to precipitate as a quickly cooled mist of sulphuric acid. This sulphur always contained some arsenic, and had therefore to be completely removed; this was attained by thoroughly mixing and thus completely burning the gases by the assistance of blowing in some steam. Hereby another very important advantage was obtained, by diluting the sulphuric acid present in the gases so that it does not condense in the first iron coolers (which prevents the formation of  $\text{AsH}_3$ ), nor attacks the subsequent lead coolers when condensed to liquid acid; it also prevents the formation of hard flue-dust and obstructing crusts in the flues and coolers.

In the patents the purifying process is described as follows:—

The hot gases are treated with a jet of steam in the dust-flue; they are then gradually cooled by being passed through a flue and then into a set of lead pipes, arranged to act as a cooler, where the temperature is lowered to about  $100^{\circ}\text{C}$ . They are then passed through a series of mechanical washers, the water in which becomes converted into dilute sulphuric acid. Such washers act incomparably better than washing-towers. The gases are finally dried by concentrated sulphuric acid. Before they pass on to the contact-apparatus, they are subjected to an optical and a chemical test. The former consists in examining a layer of the gas some yards in length, illuminated at the further end, to see that it is free from dust and mist. The chemical test is performed by passing the gas for twenty-four hours through water, and then examining the liquid for arsenic by the Marsh test.

[According to their Ger. P. 159971, the Badische Fabrik purifies burner-gases from arsenic by means of clay. Clay, especially in the unburnt state, retains not merely ordinary flue dust, and therewith great part of the arsenic contained in the gases in the shape of dust, but also the arsenic present in the state of vapour. This action greatly increases with the temperature; unburnt clay at  $350^{\circ}$  to  $400^{\circ}$  retains twenty or thirty times more arsenic than at ordinary temperatures. The temperature actually employed is about  $200^{\circ}$ . Besides arsenic also other substances, injurious in the contact-process for  $\text{SO}_3$ , are retained by the clay.]

We now come to another important principle of the Badische system, *the removal of the injurious excess of the heat of reaction*. The process  $\text{SO}_2 + \text{O} = \text{SO}_3$  produces 22,600 calories. In Lunge's *Sulphuric Acid and Alkali*, 2nd edition, vol. iii., p. 815, the following paragraph occurs:—"At a large German works pure  $\text{SO}_3$ , obtained by the Schröder and Hänisch process, or in some other way, is mixed with the necessary quantity of air; the mixture is heated to the required temperature in a pipe-stove, and is then passed through an apparatus containing clay-balls impregnated with platinum black, similar to a Deacon decomposer. This apparatus requires no external heating, since the gaseous mixture develops heat in the combination of  $\text{SO}_2 + \text{O}$ , and needs only to be protected from cooling. It is asserted that, by employing strong pressure by means of bronze

blowing-engines (air-compressors), it is possible to make  $\text{SO}_3$  directly from pyrites-burner gas cheaply enough to employ it for bringing chamber-acid up to the strength of 'rectified oil of vitriol,' in lieu of concentration by evaporation, or even to manufacture ordinary sulphuric acid in this way, and thus to do away with lead chambers."

But this refers to a highly concentrated mixture, containing about 25 per cent. (vol.) of  $\text{SO}_3$ , and could not be applied to gases three or four times more diluted. Such gases were universally believed to require not merely protection of the contact-apparatus from cooling, but heating it up to red-heat. Consequently the apparatus at the Badische was first provided with a heating arrangement. It was formed of vertical pipes, somewhat narrow, as in these the platinised asbestos can be more uniformly distributed than in wider, horizontal pipes or boilers.

The contact-furnace hence consisted of a bundle of narrow pipes, the lower half of which was filled with contact-substance, as shown in Fig. 489 (taken from the patent specification). When this furnace was started in the ordinary way at a low red-heat, it was found, against all expectations, that not merely the yields were better, but the velocity of the gaseous current could be essentially increased, if, in lieu of hot fire-gases, *cold* air was introduced between the pipes and the temperature loss thus kept essentially lower. This led to another way of proceeding. In the beginning the two fires *h* and *h'* were used, but as soon as the furnace was at work, the lower fire *h* was put out and cold air was passed along the contact-pipes, thus both cooling the pipes and performing a preheating of the cold gases entering the pipes by means of the heated current of air rising up; the fire *h'* had only to complete this preheating. In this way only the upper layers of the contact-mass became gently red-hot, and a proper temperature for the completion of the reaction was attained throughout.

In this simple manner the work was performed for several years; the temperature can be noted without a pyrometer by merely observing the appearance of the bundle of pipes. But it was found later on that the quantity of heat which could be withdrawn from the contact-process was so great that it is possible to employ the roasting-gases themselves as cooling-gas,

and thus to utilise the excessive heat of reaction for heating up the cold roasting-gas. This is done in the apparatus shown in Fig. 490, where the arrows indicate the way which the gases take. Within the brickwork M M an iron cylinder S S is arranged, with top cover W and bottom piece W', and pipes R R passing through the diaphragms D D'. The whole can be heated up to the temperature of reaction by a fire, etc., at *h h'*; the gases of

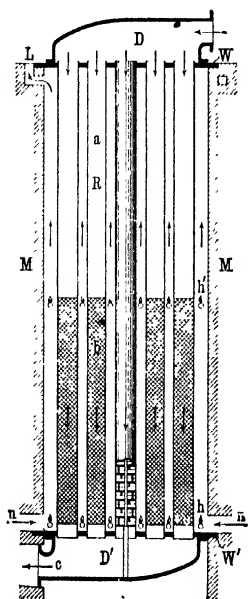


FIG. 489.

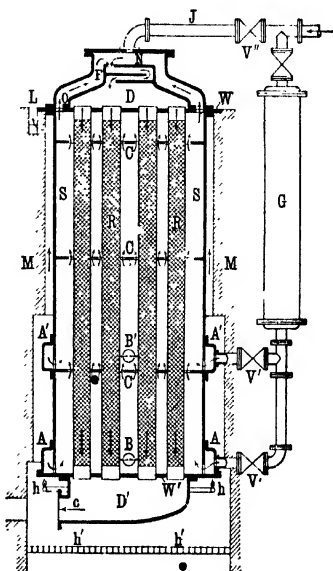


FIG. 490.

this fire escape at L. The burner-gas to be treated passes first through the heat-regulator G, then through the valves V Y' into chambers A and A', which supply the whole circumference of S with gas, as well as the radial pipes B B', which are provided with holes of a size varying according to the length of the corresponding chord of the circle, so that the gas is divided uniformly all over the system.

In order to lead the gases further on in the requisite way and to bring them as near as possible to the contact-mass to be

cooled, a number of diaphragms C C are provided, which force the gases to travel close to the pipes R R. The gases are again thoroughly mixed before entering into these pipes through O and F, and acting upon the mass by means of the baffle-plates in chamber N.

The velocity and temperature of the gaseous current is regulated by thermometers placed at D and D', and by analysis of the entering and issuing gases, until these yield the best results. If needful, other cooling-gas or air may be admitted through V'' and J. In the pipes R R the contact-reaction takes place, the heat generated in excess being transferred to the gases playing round these pipes, which are thereby heated up to the temperature of the reaction. The transformed gases issue through D' into chamber W' and proceed through G to the absorbers; but they may also be carried through the heat-regulator G, where they give up part of their heat.

The patent specifications contain a number of other forms of apparatus for applying the same principle.

There is also a specific example quoted to show how the best result can be obtained, but this applies to gases not obtainable from ordinary pyrites-burners, viz., such containing 12 per cent. (vol.)  $\text{SO}_2$  and 12 per cent. O. The apparatus is heated up by the gas-flames at  $\frac{1}{2}$  until a thermometer in D shows  $300^\circ \text{C}$ ., and the whole gaseous current is now allowed to enter at A. By constantly testing the entering and issuing gas the practical effect is ascertained, and the temperature in the contact-space, which is observed by thermometers in D and D', is regulated by means of admitting the cooling gas through valves V, V', and V'', if necessary by help of the preliminary heater G, under such conditions of heat and quantity that the maximum conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is attained. In the present case about two-thirds of the gas is introduced at A and one-third direct through J, so that, after passing the mixer N the gas in D shows a temperature of  $380^\circ$ , the thermometer in D' showing  $234^\circ$ . The conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is = 96 to 99 per cent., if 40 to 50 kg.  $\text{SO}_3$  are made for each pipe in twenty four hours; the yield may rise to 99 per cent. if the gases are left in contact with the catalyser for a longer time.

This cooling system furnishes four important advantages:—

1. There is no overheating of the apparatus, and a temperature

is obtained suitable for the highest possible yield of 96 to 98 per cent. 2. The iron apparatus is protected from being destroyed by burning. 3. The contact-mass is protected from overheating and retains its activity for years. 4. The absolute amount of work done by the contact-mass, and therefore by the whole apparatus, is very considerably increased and brought to its upper limit, because fresh quantities of gas can always be introduced without overheating and the contact-mass is kept at a temperature most suitable for its maximum effect. Hence, if the furnace gets too hot, it is not necessary, as before, to diminish the gaseous current to be treated, but its cooling action is regulated by changing its quantity or its temperature when entering the cooling-jacket, or the place where it enters, etc.

An essential point in the new process is that it is carried on without applying high pressure. Formerly it was believed (p. 1296) that the influence of indifferent gases militated against quantitative action, and that this should be compensated by employing the gases in a highly compressed state. But such an influence is absent or at least practically *nil*. There is no difficulty whatever in reaching an almost quantitative conversion of  $\text{SO}_2$  into  $\text{SO}_3$  without any excess of pressure, which means a considerable saving.

On the other hand, the gas should be made to penetrate the contact-mass very thoroughly. Loose platinum asbestos gets easily compressed too much to allow the gases to penetrate. The apparatus shown in Fig. 491 allows of working with a minimum of pressure without leaving the gases any other way except through the contact-mass itself, or hindering the cooling of the contact-pipes. The contact-mass is spread on perforated plates, strung on a central round iron spindle; small bits of pipes or pins keep the single plates apart and prevent the pressure of one layer upon another, so that there is but very little resistance to the gases, and a correspondingly small mechanical force required for propelling them. Every pipe can also be brought to a certain pressure, uniform for all of them and capable of being measured, so that the whole apparatus, although consisting of many pipes, offers an absolute guarantee for a uniform division of the gases and therefore the most normal progress of the reaction.

The best way of performing the above is described in Ger. P. 119059. Pipe R (Fig. 491) contains a central spindle *a* resting on the bottom of the apparatus and serving as guide for the following parts. On this is put a pipe *b*, reaching into the contact-pipe. Upon this is dropped a perforated plate or sieve *c*, upon which enough contact-mass is spread to cover not merely the holes, but also the space between the edge of the sieve and pipe R. Now a small bit of pipe *d* is dropped over *a*, on this again a perforated plate *c'*, and this is continued until

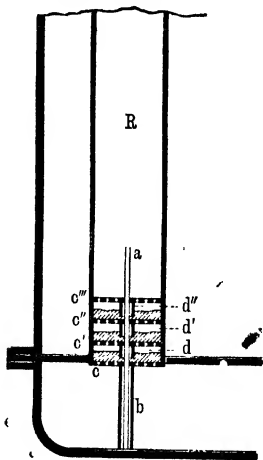


FIG. 491.

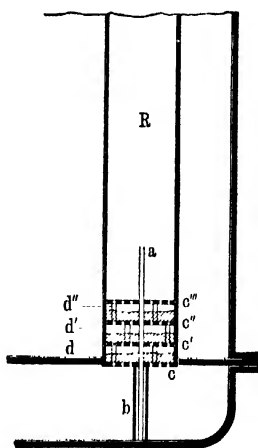


FIG. 492.

there is enough contact-substance in the pipe. Or else, in lieu of pipes *d*, the sieve-plates are kept apart by small tripods, as in Fig. 492.

A later patent of the Badische (B. P. 6828 of 1901) describes the formation of a "carrier" (in place of asbestos) by the intermediate action of an intimate mixture of an oxide or hydrate of a fixed alkali or alkaline earth, or salts of these containing a volatile acid (HCl, CO<sub>2</sub>, acetic acid, etc.), with a salt of a volatile base, such as ammonia, and a less volatile acid, such as sulphuric or phosphoric acid, at a suitable temperature. At such a temperature double decomposition takes place, and the vapours of the volatile salt so formed on escaping impart a high degree of porosity to the non-volatile

salt remaining behind. The platinum may be added to the mass either before or after heating.

Another B. P. of the same firm (12781 of 22nd June 1901) states that half of the platinum or more, up to 70 per cent., can be dispensed with by dividing the process into two stages, and removing the  $\text{SO}_3$  formed in the first stage before submitting the gases to the second stage. Otherwise, with 100 parts of platinum and a total conversion of 97 per cent., the production of the first 80 per cent.  $\text{SO}_3$  only requires 15 parts of the total platinum employed, while for the remaining 17 per cent.  $\text{SO}_3$  85 parts of platinum are necessary. But if, after in the first phase converting 80 per cent. of the  $\text{SO}_2$  into  $\text{SO}_3$ , the latter is removed by absorption and the remaining gases are again submitted to contact-action, the formation of  $\text{SO}_3$  proceeds again with the same velocity as at first, so that the total conversion is  $= 80 + \left(20 \times \frac{80}{100}\right) = 96$  per cent.

This is sufficient for practical purposes, and it takes only  $15 + 15 = 30$  parts of the platinum necessary for a direct conversion of 96 per cent. In the same manner it is possible to rise from 80 per cent. in the first phase to 98 per cent., or from 90 per cent. in the first phase to 99 per cent. total conversion.

The Ger. P. 148196 of that firm states that the platinum contact-mass, when rendered inactive, can be revived, by means of dry sulphur dioxide, either by itself or mixed with other gases containing little or no oxygen, passed through the mass at the temperature of the contact-process. Thus no impurities are introduced into the mass, and, owing to the dry state of the gas, the apparatus is not damaged.

Last of all we must allude to the question of *absorbing* the sulphur trioxide contained in the gases. It is well known that  $\text{SO}_3$  has much more affinity to water than to concentrated sulphuric acid; in the former case 1 kg.  $\text{SO}_3$  liberates 500 calories, in the latter (1 kg.  $\text{SO}_3$  with an excess of sulphuric acid 66° Bé) only about 300 calories. It would therefore be the most natural thing to arrange a number of vessels in such manner that the absorbing acid is gradually less concentrated in the direction of the gaseous current, that water or dilute acid is run into the last vessel, and that fuming acid or acid of any other desired commercial concentration is run out from the



first vessel. Against all likelihood such an arrangement does *not* produce the maximum of work. On the contrary, it is very difficult to absorb  $\text{SO}_3$  by means of water or dilute sulphuric acid; considerable quantities of whitish mist still escape from the apparatus, causing loss (and nuisance). But it has been found that at a certain concentration, between 97 and 98 per cent.  $\text{H}_2\text{SO}_4$ , sulphuric acid has the property of absorbing sulphur trioxide completely and momentarily. (This peculiar property of acid of that special concentration, together with its other remarkable properties, has been described on p. 292, where also Sackur's explanation of the phenomenon described by Knietzsch is given.) It is thus possible to remove all the  $\text{SO}_3$  out of the gaseous current by a single absorbing-apparatus, in which the concentration of the acid is kept between 97 and 98 per cent.  $\text{H}_2\text{SO}_4$ , by continuous feeding with water or dilute acid, and continuous running off of the excess of strong acid formed.

If *fuming* acid is to be made, one or more absorbers are placed in front of the last. Here again very peculiar phenomena are observed. Whereas in the manufacture of hydrated sulphuric acid cast-iron vessels are very suitable, this is not the case with fuming acids, which do not corrode the cast-iron very much, but cause it to crack (*cf.* p. 323). Wrought-iron is strongly corroded by fuming acids of less than 27 per cent.  $\text{SO}_3$ , as is explained by its electric conductivity (p. 324). Above 27 per cent.  $\text{SO}_3$  the acid renders wrought-iron entirely passive, and such apparatus can be used for many years for the manufacture of *strongly* fuming O.V., above 27 per cent.  $\text{SO}_3$ . Thus also fuming acid almost entirely free from iron can be made (0.003 to 0.001 per cent. Fe).

The U.S. P. of R. Knietzsch, 692018, of 28th January 1902, contains a synopsis of the various operations, as shown in "Fig. 493. Sulphur dioxide is taken from the supply A through the drying-train B into the "induction separator" C, in which the gas is mixed with air from the pump D; the mixed gases then enter the washer E, a leaden vessel from the top of which is suspended a hood having serrated edges dipping into sulphuric acid of 66° B $\acute{e}$ .; a pressure-gauge affixed to the entrance and another to the exit show the respective pressures. The gases then pass through the

salt remaining behind. The platinum may be added to the mass either before or after heating.

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# 1340 MANUFACTURE OF FUMING OIL OF VITRIOL

"stripper" F, formed similarly to the washer, but containing no liquid except such sulphuric acid as may be deposited by the gases, which next enter the contact-chamber H and then

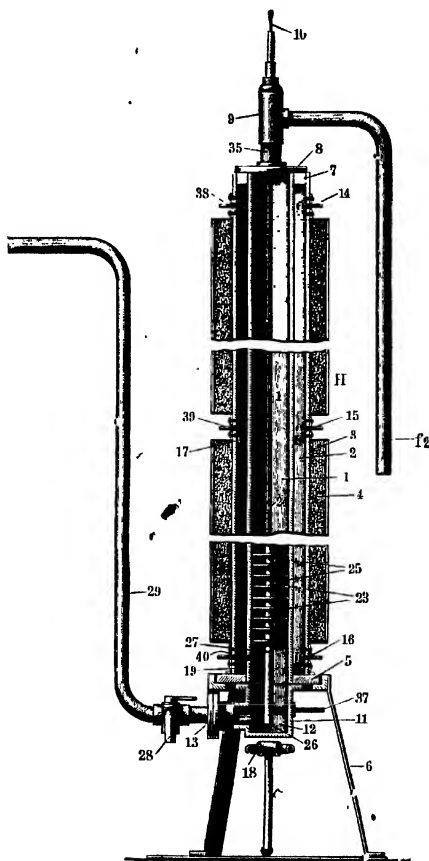


FIG. 494.

the absorber I of wrought-iron (having a serrated suspended hood of the same metal containing sulphuric acid of 66° B $\acute{e}$ ., which thus becomes fuming acid by absorption of SO<sub>3</sub>). The absorber I is immersed in a cooling-vessel. The second absorber J is of a similar construction, but is made of cast-iron;

it contains sulphuric acid of 58° Bé., which, when brought up to 66° Bé. by the  $\text{SO}_3$  reaching it, is available for recharging absorber I. G and K are testing-apparatus.

The contact-furnace H is separately shown in Fig. 494. I is a central tubular contact-chamber, jacketed by the annular passage 2 and surrounded by insulating material 4. The sheet-iron tube 3, forming the annular passage, is pierced to form a series of portholes, 14, 15, and 16, each series being provided with two independent semicircular covers, 38, 39, and 40, governing separate halves of the series, by which admission of air for regulating the heat is controlled, the heat being supplied from the gas-burner 18 and the annular burners 17 and 19. The mica-covered peep-holes, 22, enable observations to be made of the colour attained within, which should be a dull red opposite the upper portion of the contact-material. Directions are given for regulating the temperature as indicated at 10, 14, and 37. In the contact-material holder, the rod 24, removable from the top on withdrawing the cover 8, has strung upon it a series of perforated iron plates, 23 (Figs. 495 and 496), distanced by sections of piping, 25, and the bottom plate is distanced from the nut 26, on the bottom of the rod, by the section of piping 27; this latter section in charging the apparatus is dropped down the rod followed by a perforated plate, on to which is scattered a certain quantity of 10 per cent. platinised asbestos; one of the piping sections is then dropped into position and a perforated plate, and so on until the apparatus is charged. This apparatus is stated

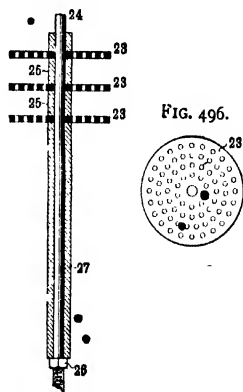


FIG. 495.

to have accomplished an average conversion of 95.9 per cent. while making sulphuric anhydride at a stated rate, the gases used containing 11.5 per cent.  $\text{SO}_2$ .

The Ger. P. 140353 and B. P. 10729 of 23rd May 1901 of the Badische Anilin- und Sodafabrik prescribes the use of the oxides of iron, copper, or chromium as substrata for platinum black, to be produced per example, as follows:—145 parts. of burn-

## 1342 MANUFACTURE OF FUMING OIL OF VITRIOL

pyrites, entirely free from arsenic (this is essential), in pieces about the size of a pea, screened so as to be free from dust, are impregnated with 30 parts of a solution of platinum chloride containing 17 g. platinum to the litre. The resulting product can be used at once as a catalyser, or may first be heated. Such bodies are not molecular mixtures like those obtained by means of organic fabrics (*cf.* Porter's patent *infra*, p. 1431), but are formed of granules of metallic oxides covered with a layer of platinum. The catalytic action of the platinum is supported or increased by that of the oxides, and the product acts at least as well as platinised asbestos. These contact-bodies are cheap, offer great resistance to heat and chemical action, and require no special arrangements for preventing the pressure on the contact-material from forming an impermeable mass.

The annual production of sulphuric anhydride at the Ludwigshafen works of the Badische is stated by Knietsch:—

In 1888 = 18,500 tons.

„ 1894 = 39,000 „

„ 1899 = 89,600 „

„ 1900 = 116,000 „

The Badische Anilin- und Sodafabrik declares, in *Z. angew. Chem.*, 1905, p. 97, that the process employed by the Tentelewsche Chemische Fabrik is not, as asserted by Suler in the *Transactions of the 5th International Congress for Applied Chemistry*, vol. i. p. 476, an invention of that firm, but is identical with theirs, and has been communicated to the Tentelew works by a person who had obtained cognisance of it in an illegal way. An answer to this by the Tentelew Company and a final reply by the Badische appeared in *Chem. Ind.*, 1905, pp. 178 *et seq.*, and, in *Z. angew. Chem.*, 1905, pp. 379 *et seq.* Against Winteler, who (*ibid.*, 1906, p. 237) had criticised the originality of their Ger. P. 113933 (corresponding to R. Ps. 15947 to 15950 of 1898), the Badische upheld the originality of this patent, *ibid.*, p. 334.

The Aktiengesellschaft für Zinkindustrie vorm. Grillo, in *Z. angew. Chem.*, 1906, pp. 712 *et seq.*, contends that Clemens Winkler had already recognised the injurious effect of arsenic in the contact-process<sup>1</sup>; that their firm had already in 1886

<sup>1</sup> I must doubt this fact, for which the above firm in fact adduces no proof whatever. *Cf. supra*, pp. 1287 *et seq.*—G. L.

mentioned this effect in a letter to the Badische, although they did not consider arsenic quite as damaging to the contact-mass as silicon-fluoride, HCl or chlorine. The injurious effect of arsenic is probably owing to the formation of a thin pellicle on the contact-mass, as asserted by Opl.<sup>1</sup> They assert that all SO<sub>3</sub> factories not directly arranged by the Badische employ the filtration of the gases as a sufficient purifying agent, *not* the washing of the cooled gases, or the blowing-in of air or steam.

The following communication, made to me directly, by the Badische Anilin- und Sodafabrik, is here given in a verbatim translation.

*Contribution to Lunge's Text-book, Third Edition.*

In a lecture delivered before the German Chemical Society (cf. *Ber.*, 1901, vol. xxxiv. p. 4079), R. Knietsch has already made detailed communications as to inventions of the Badische Anilin- und Sodafabrik in the field of the manufacture of sulphuric acid by the contact-process, and as to the position which must be attributed to these inventions in the general history of the contact-process. The following additional facts are supplied at the desire of the author of this book by way of supplement to the publication mentioned.

We originally procured the fuming sulphuric acid that we required for the production of our colouring-matters from J. D. Starck in Bohemia, as did also all other colour factories. In the year 1875, Winkler published his epoch-making proposal to use the mixture of SO<sub>3</sub> and O in their combining proportions, as obtained by the decomposition of ordinary concentrated sulphuric acid at a red-heat and removal of the aqueous vapour, in the manufacture of fuming sulphuric acid according to the contact-process by passing the mixed gases over platinised contact-substances. We at once adopted this process, but there were such considerable difficulties in effecting the process on the manufacturing scale that we proceeded to experiment with

<sup>1</sup> Opl (*Chem. Zeit.*, 1905, p. 757) ascribes the "poisonous" action of arsenic in contact-processes exclusively to the formation of a compound of As<sub>2</sub>, O<sub>3</sub>, and SO<sub>3</sub>, which decomposes with formation of a glass-like coating on the platinum, and thus acts purely mechanically. That compound, to which he ascribes the formula:—3As<sub>2</sub>O<sub>3</sub>, 2SO<sub>3</sub>, has been actually found in dust-chambers.

burner-gases. These experiments were begun in the year 1881, as we can see from our records, and were carried on uninterruptedly, although for a time we were licensed to use the process of Schröder and Hänisch, which starts from gas containing approximately 100 per cent. of sulphur dioxide. This process was tried, but subsequently dropped.

The introduction of the use of burner-gases in the contact-process required the solution of a series of further preliminary problems, and the very unfavourable results which were at first obtained were really such as to leave but little hope of any success when using burner-gases, and the idea of replacing the lead-chamber process by the contact-process was apparently altogether out of the question. At that time it would have been regarded as highly satisfactory if it had been possible when using burner-gases to replace the complicated and expensive Winkler process for producing fuming sulphuric acid by a simpler and cheaper process. The turning point in our experimental work was only reached when R. Knietzsch in our laboratory made the pioneer inventions, which are described in the lecture already referred to (cf. *suprà*, pp. 1327 *et seq.*). These were based upon entirely new observations and experimental results.

As stated in the lecture, there are inventions with reference to all the stages of the contact-process, especially with reference to the preliminary treatment of the gases (absolute purification from deleterious ingredients), to the actual contact-process (cooling the contact-mass and working without pressure and apparatus for these purposes), and to the absorption. The technical success of these inventions entirely surpasses anything that was deemed possible from the state of the art at that time, as shown by the literature of the subject and by the results obtained in practice. These inventions have resulted in the possibility not merely of producing fuming or ordinary concentrated sulphuric acid far more cheaply than was formerly the case, but, further, it is possible to substitute with advantage the contact-process for the lead-chamber process in the manufacture of ordinary chamber-acid.

It is sufficient for us to refer to the report of the lecture in the *Berichte* for the details of the invention, and in this report the literature of the subject and the views that were taken

by technical men are summarised.<sup>1</sup> By way of supplement to the literature there noticed, we will here only mention that all that was known of the process carried out at Freiberg previous to the lecture of Winkler in Hanover in 1900 (cf. *Z. angew. Chem.*, 1900, p. 731) is the communication of Schnabel in his *Text-book of General Metallurgy*, 1st ed., 1890, p. 516. The passage runs as follows:—

"The fumes from the calcining-furnaces, which can be used for the manufacture of sulphuric acid, can also be employed for the production of sulphuric anhydride. This is effected at Freiberg with a small proportion of the roaster-gases. These are at first dried by passing them up towers whilst a spray of concentrated sulphuric acid descends in the opposite direction; then the gases enter closed heated vessels containing the platinised asbestos. Here, in consequence of the catalytic action, sulphuric anhydride is formed from the sulphurous acid and oxygen. The fumes containing the anhydride then enter a tower in which concentrated sulphuric acid drips down and absorbs the anhydride, and the anhydride is distilled off from the liquid so obtained. The gases leaving the absorption-towers still contain sulphurous acid. This is passed into the lead-chambers together with the other burner-gases intended for the manufacture of sulphuric acid. The earlier experiments on the conversion of sulphurous acid from the calcining-furnaces into sulphuric acid by catalytic action had a negative result until Winkler introduced the process described."<sup>2</sup>

By the introduction of our invention into our factory on the large scale, we have been in a position since the early nineties to outdo our competitors in the home market, not only with fuming, but also with concentrated sulphuric acid. But the attainment of the great object which we deliberately

<sup>1</sup> It is, however, unfortunately the fact that, even in text-books published since the lecture, mistaken descriptions are given of the fundamental principles and the nature of our inventions. (See, for instance, the latest edition of the *Text-book of Chemical Technology* by Ferdinand Fischer, published in 1903.)

<sup>2</sup> We take this opportunity of remarking that this passage reappears in similar form in the second edition of *Schnabel's Text-book* just issued, 1903, p. 584. There is the further information that when using this process only about half of the sulphurous acid contained in the gases was converted into anhydride. After this, the advances secured by our process are discussed



aimed at, namely, to improve the new process so that even for the manufacture of ordinary dilute sulphuric acid it should become superior to the lead-chamber process, required still further energetic work.

During this period of the development an event occurred which threatened to deprive us of a great part of the fruits of the labours which we had been carrying out with such great pains for many years, and, to a certain extent, we must admit that we have suffered loss. Our first intimation as to the matter referred to came from various factories that supply us with our apparatus. They informed us that a Dutch factory for the manufacture of sulphuric acid had ordered apparatus for the manufacture according to the catalytic process, and the drawings sent in showed that part of the apparatus required was identical with, and partly agreed in essential points, the peculiar sulphuric-acid apparatus that existed solely in our factory. There could be no doubt that there had been a betrayal of our factory secrets, and we immediately suspected a mechanic, Carl Daub, who had been engaged in mounting the plant of a new sulphuric-acid factory, and had been dismissed from the works towards the end of 1895. This suspicion has proved to be fully correct, for it was found that this workman whilst in our factory systematically spied out our sulphuric-acid process, which was treated as a strict secret, as far as he possibly could. He also made copies of drawings and the like. Together with his brother Friedrich Daub, who was engaged as a chemist in the Dutch factory referred to, and who assisted him in formulating the questions to be put to the workmen in the sulphuric-acid department, he endeavoured to make capital out of his illegitimate knowledge, and immediately after leaving us he entered the Dutch factory. After this Friedrich Daub sent offers to all important sulphuric-acid factories here and abroad, offering "his" process for sale, and explaining that it was identical with that carried

p. 585 (compare a careful purification of the roaster-gases from all admixtures which are deleterious in the process and a suitable arrangement of the contact-apparatus). It is true that our name and our patents are not mentioned, and there is the further remark that the production of chamber-acid by the contact-process is dearer than by the chamber-process, but the additional explanations that we give will show this statement is not true in the general form in which it is made.

out by us. Later on he advertised quite openly in the trade papers. Although the circumstances and, in part, the nature of the communication offered could leave little doubt, in the minds of all concerned in the matter, that this was a case of betrayal of factory secrets, nevertheless several factories entered into negotiations and received in the correspondence that followed, or in the verbal negotiations, the assurance that Carl Daub had been engaged in our factory for several years and had a "most thorough" knowledge of our apparatus, and that "although the drawings had perhaps not been obtained in the most respectable ('nobel') manner, still it was not to be feared that the Badische Anilin- und Sodafabrik could take any steps." In this connection drawings which agreed more or less with our arrangements were laid before the would-be customers under the condition of secrecy.

It is hardly within the scope of this communication to mention the steps that were taken against the brothers Daub, and with reference to the firms who were in negotiation with them. We will only mention that amongst other things we sent a circular to all interested parties, and in this way, in a number of cases, the negotiations that had been begun were broken off, whilst, on the other hand, a few firms, amongst them the Dutch firm mentioned and other sulphuric-acid factories abroad, entered into agreements with the brothers Daub and were not ashamed to acknowledge this.

Fortunately, the information as to our process which the Daubs had obtained by spying was imperfect, and in part false, probably especially owing to the dismissal of Daub before he had fully ascertained our secrets, and owing to the fact that his intention to carry on further correspondence with our workmen was frustrated. Still, the practical success of our inventions, as also, for instance, the existence of contact-stoves which work automatically and of our effective purification-plant for burner-gases, became known through the treachery of Daub. The certainty that there was a process of such efficiency that it was possible to replace the chamber-process was alone sufficient to excite a large number of persons to the endeavour to obtain for themselves a share in the new achievements. Ideas and plans which had been partly or entirely abandoned, as no practical success could be hoped

from them, were immediately reconsidered, after it became known that such success was really possible, and from that time on a flood of patent applications set in in all countries. It was therefore obviously desirable in our interest to draft immediately an account of our work and publish it in the form of patents; but after we had published the fundamental inventions in this way, and after the greatest difficulties had been overcome, those inventions had the look of being very simple and clear, and the phenomenon recurred which has been observed in the case of so many epoch-making inventions, namely, that others who had worked with less success now saw clearly the essentials for success. The causes of failure of their own experiments and the reasons for our successes and our process itself now appeared quite a "matter of course," and this the more readily, because it is a fact that many ideas of similar nature had from time to time been under consideration, although indeed, on account of the apparent hopelessness of the problem, they had not been worked out in detail. As a consequence, in the oppositions that were raised against the grant of our patents, the statement was made again and again that the processes described and the observations and experiments on which they were based were not new, and even where processes had to be acknowledged as novel, still in some cases they were described as "almost obvious and a matter of course." This is absolutely unjustified, as is already obvious from the universally acknowledged pre-eminent success achieved by our processes, which has been characterised by Clemons Winkler as "weltbewegend"—an expression difficult to translate, but which implies the creation of a sensation throughout the world (see *Z. angew. Chem.*, 1900, p. 737).

We will in the first place deal with the perfect purification of technical gas mixtures containing sulphurous acid (especially burner-gases) up to a point defined by us at which an optical and chemical test is satisfied (Ger. P. 113933; B. P. 15948 of 1898; Amer. P. 687770). It appears on the face of these patents that before our invention not even the necessity for the absolute purity of the gases in the defined sense was recognised, and further, of course, no means were known for carrying the purification to such a high degree. The necessity for such purity, and the means to be adopted for

achieving it, could not be known, because it was first necessary that the deleterious action of some of the admixed impurities should be recognised, and some of these impurities, such as small quantities of sulphur or sulphuric-acid mist, owing to their nature, and, further, traces of arsenic, on account of its volatility at the temperature of the contact-process, could not be regarded as in any way dangerous. Before the specific poisons for the platinum contact-apparatus, in particular arsenic, had been discovered, and the fact that sulphur and sulphuric-acid mist served as carriers for these contact-substance poisons, and acted in just as deleterious a manner on the contact-mass, there was absolutely no reason to consider means for fully removing these substances, and these considerations had greater force because it was generally believed that when working with technical burner-gases from pyrites it was in the nature of things impossible to achieve a quantitative conversion of the sulphurous acid into  $\text{SO}_3$ .

But even after the necessity for this absolute purification from deleterious ingredients had been recognised, a great step was necessary before a serviceable process for this operation could be discovered. When, therefore, the necessity for this perfect purification of the gases and means for effecting the operation were subsequently declared by third parties to be known or almost obvious, it must be borne in mind that prior to our invention the purification of burner-gases had in no case been carried further than the removal of coarse impurities (the greater quantity of the flue-dust), whilst the complete removal of flue-dust and of the admixtures in the contact-gases which at high temperatures exist in the form of vapours, mist, or gases had not been achieved in cases where it had been attempted, at all, and in the opinion of the highest authorities on this art (Lunge, Winkler, Schnabel) was regarded as absolutely impossible.<sup>1</sup>

<sup>1</sup> Immediately before our application for a patent for this process was filed, there was one in full accordance with this view (patent 102204 of 17th May 1898, of the Aktiengesellschaft für Zinkindustrie, vorm. Grillo in Oberhausen, and Dr. Max Schroeder, Düsseldorf). The application referred to the production of contact-bodies that could be readily regenerated, and as the reason for the invention the statement is made that "the burner-gases always contain some flue-dust, even after careful purification, and consequently, in course of time, the contact-bodies become covered with a layer

We have been confronted with the process for the production of pure sulphurous acid from burner-gases of the Ger. P. 26181 (Hänisch and Schröder); but this has nothing in common with our process for purifying the burner-gases, for, quite apart from the complicated and expensive method of absorbing the sulphurous oxide in water and then expelling it again by boiling, this process does not on the one hand in any way involve the same fundamental intention as ours—namely, to remove from the burner-gases just those substances which are deleterious, which, however, at that time were not even known to be deleterious. Again, according to this process, which had for its end the production of pure sulphurous acid for other purposes, concentrated sulphurous acid containing nearly 100 per cent.  $\text{SO}_2$  is obtained, and in order to make this applicable for the contact-process this has to be mixed with oxygen or air, whilst according to our process, apart from the deliberately purposed removal of all deleterious impurities, they are not changed in their composition, but contain  $\text{SO}_2$ , O, and N in the same proportions.

We will now deal with another constantly recurring objection, viz., the fact that it had already been observed that arsenic has a deleterious action on platinum sponge as used in the Döbereiner igniting-apparatus. Those who wished to regard this as affecting in any way the novelty of our process ignored the fact that this little apparatus not only deals with quite a different chemical process from that under consideration, but also that in this igniter the platinum has to become heated from the temperature of the air to the temperature at which hydrogen ignites, whilst the requirements in respect to temperature in the contact-process in the manufacture of sulphuric acid are altogether different. Analogy cannot be relied upon in this

of almost impervious matter, and this diminishes their effect." The applicants for this patent had, however, in no way apprehended the existence of the specific poisons for contact-substances, such as arsenic, which were discovered by us, and, even after our inventions were published, the firm named directly contended that arsenic was not injurious to the contact-mass. (Cf. *J. Soc. Chem. Ind.*, 1903, p. 350.)

[According to a new Fr. P. of the Badische, 414387, the purification of the gases is greatly simplified by reducing the  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  they contain to  $\text{SO}_2$ , which is performed by passing the gases at a temperature of about  $425^\circ$  through pieces of gas-coke of the size of a man's fist.—G. L.]

field of work ; for instance, palladium, which belongs to the same group of elements as platinum, behaves towards hydrogen in a similar manner to it, while it is practically altogether inapplicable for the union of  $\text{SO}_2$  and O.

We can state with satisfaction that the German Imperial Patent Office accepted our arguments as to the novelty of our process and the observations upon which it is based, and granted us the patent for the purification process without any limitations, as applied for by us, rejecting the oppositions in both instances.

In view of the fact that the means devised by us for effecting the purification were new, and based on the discovery of new fundamental principles, it is a matter of course that other and similar means of achieving the purification should fall within the scope of our patents. Our process, for instance, can be carried out in such a way that the intimate contact of the gases and the washing-liquid is brought about, instead of by washing, as we had done, by the essentially identical process of wet filtering. We have already used this process with complete success for the process in question (cf. *Ber.*, xxxiv. p. 4081).

It has also been urged against our cooling-process (Ger. P. 113932 ; B. Ps. 15497 and 15949 of 1898 ; Amer. Ps. 652119 of 1900 ; 688020, 688469 to 688472, 690062 of 1901 ; and 692018 of 1902), in the oppositions that were raised against the grant in Germany, that it was destitute of novelty and almost obvious.

The novelty and originality of the cooling-process can be seen at once from the state of the art as shown in the literature at that time. It appears from the literature that it was known that the contact-process could only be effected at an elevated temperature, and that it was consequently necessary to heat the apparatus, and, with reference to the temperature of the contact-substance, the only point to which attention had been called was economy of fuel. For this purpose endeavours were made to avoid a special heating of the contact-apparatus by surrounding it with heated gases whose heat would otherwise have been lost. Or, again, the gases entering upon the reaction were permitted to enter the contact-apparatus at a sufficiently high temperature to make a further heating unnecessary (cf. second edition of this text-book, vol. iii. p. 815). In this connection it must be borne in mind that the apparatus described in that

place<sup>1</sup> was intended for working up gases containing about 25 per cent. of  $\text{SO}_2$ , and not for burner-gases, so that the heat of reaction developed in this case would have caused a far higher rise of temperature than that which occurs when ordinary burner-gases containing from 6 to 8 per cent. by volume of  $\text{SO}_2$  are used. Even though it is to be regarded as generally known that the temperature of the contact-apparatus should not rise "altogether too high," nevertheless there is no mention anywhere in literature of a cooling-operation, far less of any deliberate and intended cooling of the apparatus. The universal belief was that if the percentage of conversion decreased, partly owing to the action of the contact-poisons, which were then unknown, or partly in consequence of the heat of reaction causing the deleterious overheating of the contact-mass, which was also unknown, then the reason of it was that the ultimate capacity of the contact-mass had been reached, and that therefore, if the same percentage conversion was required, the current of gas must be made slower. So long as the work was conducted on these principles, namely, that of heating the contact-apparatus, or at least preventing cooling as far as possible, it is obvious that the quantity of gas that could be treated, and consequently the efficiency of the apparatus, must be relatively very limited, as can now, after the publication of our process, be readily understood by everyone skilled in the manufacture.

The apparatus described in the B. P. 3166 of 1888 (Ellice-Clark) also employs the principle above mentioned of heating the contact-apparatus, and in this case the heating was effected by the waste heat of the pyrites-burners. In this patent, which is only mentioned casually in the second edition of this book, the inventor, George Lunge, directs that "the temperature in that part of the apparatus where the union of  $\text{SO}_2$  and O takes place must be carefully regulated, and not to be too high or too low, preferably at or under a dark red-heat." This corresponds simply to that which was known up to that time in this respect (*cf.* Squire's B. P. 3278 of 1875). The contact-tubes, even though their temperature is to be regulated, are in this case, just as in every previous case, heated by the heat of the pyrites-burners, and not in any way cooled. In this patent also there

<sup>1</sup> We should like to state that up to the present day we know of no factory in which this apparatus has ever been in practical use.

is no suggestion whatever that a special temperature favourable for the contact-process shall be brought about by cooling.

We have shown that our process, based upon the principle of cooling, is a completely new one, and opens up a course that was previously entirely unknown; but the great technical advance that is secured by the invention of the Ger. P. 113932 (B. Ps. 15947 and 15949 of 1896; Amer. Ps. 652119 of 1900; 688020, 688469 to 688472, 690062 of 1901; and 692018 of 1902) results from the fact that in place of a crude empirical method of working based upon a diminution of the efficiency of the apparatus, a quite new inventive idea and a method of working of the greatest importance are adopted, whereby the work is rationally conducted and the well-understood effects are deliberately caused. This new method of working is the regulated external cooling of the contact-apparatus; by this means the heat of reaction, which is the cause of the deleterious overheating of the apparatus and consequent dissociation of  $\text{SO}_3$ , is removed, with the result that the same quantity of contact-substance can now deal with a considerably larger quantity of gas, and the efficiency of the apparatus is raised to the highest possible degree. There is the further technical advantage that the cooling can be effected by the reaction-gases themselves, so that these need not be preliminarily heated for the subsequent conversion.

It can be seen from this that in our cooling-process the heat of reaction can simultaneously be used; but it should be observed that the method of working in using the heat of reaction, as can be seen from what has been said without further explanation, differs entirely in principle from that described in the Ger. P. 105876 (B. P. 6057 of 1898), in which the heat contained in the reaction-gases which have already left the contact-stove is used, whilst the removal of the excess heat of reaction during the reaction, and consequently the increase in the efficiency of the apparatus, cannot possibly be effected.

By the use of our cooling-process, not only is the achievement of a higher degree of conversion of  $\text{SO}_2$  into  $\text{SO}_3$  (96 to 98 per cent.) secured than has hitherto been effected, but also, and this is just as important, simultaneously the efficiency of the contact-mass is used up to its utmost limit.

But it is not to be thought that this effect is in any way



achieved by maintaining a definite uniform temperature in all parts of the contact-apparatus. In none of our patents do we prescribe the use of a definite uniform temperature; on the contrary, in the examples we quote we only mention the temperature of the gas entering and of that leaving the apparatus. In view of the nature of the contact-process and the cooling-process, especially when the cooling is effected by a counter current, it is impossible to maintain a uniform temperature throughout the contact-apparatus. If the advantages of our cooling-process with respect to the efficiency of the contact-mass are to be fully enjoyed, an exceedingly vigorous reaction will take place in the first layers of the contact-mass, in consequence of the great burden that is thrown upon them, and consequently at these first layers there is a rapid rise of temperature. By the external cooling the heat is gradually removed as the gases pass on, and so the temperature is again brought to the stage at which the most perfect conversion takes place (see also the curve showing the velocity of the reaction in the *Ber.*, 1901, p. 4098). The temperature in the interior of the contact-chamber, as employed in manufacturing on the large scale, rises rapidly to a maximum, which occurs when the gases have passed through approximately one-quarter of the contact-mass. From this maximum it gradually falls to about  $380^{\circ}$  or  $450^{\circ}$  C., between which temperatures the conversion of from 96 to 98 per cent. is possible. It is wrong, therefore, to imagine that our cooling-process proceeds as a matter of fact at any definite temperature or between narrowly limited temperatures, and the most favourable conditions of temperature must be determined for each single case. Direct observations upon apparatus that have been in use for many years past in the factory have shown that the temperature is exactly as above described in the contact-mass, and that the temperature at which the gases enter, the maximum temperature, and the final temperature may be varied within wide limits without essential alteration of the quantitative result.

If, therefore, the temperature of the various parts of the contact-space be so arranged that at first there is a low temperature, later on a more or less elevated temperature, then again a lower temperature or, indeed, if the first phase be nominally dropped so that at first the operation is conducted at a high temperature

and then at a lower temperature, these variations are nothing more or less than the actual cooling-process patented by us in the Ger. P. 113932. Of course, modifications can be made in the arrangement of the contact-mass in the tubes; for instance, the contact-mass can be arranged outside horizontal cooling-tubes through which the cooling-gases pass. In every such case the process of cooling described in our patent is used, and must, indeed, be used if the practical quantitative conversion of  $\text{SO}_2$  into  $\text{SO}_3$  and simultaneously the maximum efficiency of the contact-mass is actually to be achieved, for there is no other means of attaining this result.

The same is the case when apparatus in the form of pots or large vessels are used, if these are to be so worked as to yield what is to-day regarded as a sufficient conversion. Such apparatus, even after it is furnished with non-conducting covering, nevertheless gives off heat, that is to say, some cooling takes place. This can at once be seen in such cases where the temperature, exactly as in our process, rises at first and subsequently falls as the gases pass through the apparatus; but the cooling in these cases cannot be regulated but remains constant, so that such apparatus suffers from the disadvantage that only a certain amount of heat can be got rid of, so that each apparatus can only work with a definite quantity of gas, which must be empirically ascertained for the apparatus. As against such apparatus, the special forms described in our Ger. P. 113932 have the essential advantage that they are, within wide limits, independent of the quantity and concentration of the gases. At the same time, our apparatus when it has once been regulated for definite conditions works automatically within certain limits, so that the means for regulating need only be used again when the quantity or the concentration of the gas changes considerably. A further special characteristic of our process is that it works without pressure, and in this way the idea formerly held, namely, that a high yield of sulphuric anhydride could only be obtained by employing pressure, has been demonstrated to be false with certainty. It is true that, theoretically, the equilibrium of the action would be changed favourably for the formation of  $\text{SO}_3$  by the application of pressure; but already, at a time when the various theories of physical chemistry were but little developed, we proved experimentally that under the conditions of technical

manufacture according to the contact-process it is possible without pressure to arrive at a practically quantitative yield, and that therefore the matter of pressure is not only of no great value, but is of such slight importance that it can be absolutely neglected. Similarly the belief was held, based upon the law of action of mass, that a dilution of the gases with air had a deleterious influence, and this view was expressed by many. In this case also we proved the right way by experiment before the development of physical chemistry.

Our recognition that pressure was of no practical importance and that an admixture of the gas with air had no harmful influence, was of the greatest economic value for the contact-process, for after this it was clearly seen that ordinary dilute burner-gases could be employed and means could be devised for passing the gases through the contact-mass whilst opposing as little resistance as possible, so that the mechanical force required for moving the gases could be reduced to a minimum.

The recognition that pressure has no essential influence is the basis upon which the apparatus of our Ger. P. 119059, and the process of our patent 133713 is based (B. P. 15950 of 1898). The subject matter of these patents, as also of those referring to our absorption process, are discussed in the *Ber.* at the place already cited.

We will finally mention the only process in which another contact-material, namely, burnt pyrites, is used. The inventors of this process believed at first that they could by its use complete the reaction, but, nevertheless, they subsequently found that in a contact-stove containing iron oxide only 60 per cent. of the gases was converted in one operation, the remainder, after being completely freed from the catalytic poisons discovered by us, has then to be combined with the aid of platinum.

In the lecture reported in the *Bericht*, to which we have several times referred, the importance of our process was illustrated by mentioning the quantity of  $\text{SO}_3$  produced annually by our process (*supra*, p. 1342); since that time the production in our factory, as also in particular the production of our licencees, is essentially greater and now amounts to about 200,000 tons of sulphuric anhydride annually. This quantity is continually increasing.

(Here ends the communication to me by the Badische Fabrik.)

The following is a list of the various patents of the Badische Anilin- und Sodafabrik on the manufacture of sulphuric anhydride:—

I. For cooling the gases: B. Ps. 15947 of 1898; 15949 of 1898; Ger. P. 113932; Fr. P. 280647; Amer. Ps. 652119, 688020, 688469, and following up to 688472, 690062, 692018; Belg. P. 137751; Austr. P. 1662; Russ. P. 5897; Hung. P. 15503, and others.

II. Purification of the gases: B. P. 15948 of 1898; Ger. Ps. 113933 and 159976; Fr. Ps. 280649 and 414387; Amer. P. 822373; Belg. P. 137752; Austr. P. 1093; Russ. P. 5945; Hung. P. 25533, and others.

III. Arrangement of the contact-mass: B. Ps. 15950 of 1898; 6828, 10729 and 12781 of 1901; Ger. Ps. 119059, 133713, 140353, and 148196; Fr. P. 280648; Amer. Ps. 774083 and 823472; Belg. P. 137753; Austr. P. 1771; Russ. P. 5842; Hung. P. 15475.

IV. Absorption of  $\text{SO}_2$ : B. P. 6825 of 1901; Ger. P. 133933; Fr. P. 309673; Amer. P. 816918; Belg. P. 158923; Austr. P. 10675; Russ. P. 8504; Hung. P. 25574.

V. Fuming O.V. absolutely free from iron: B. P. 1904 of 1901; Ger. P. 133247.

## II. *Processes of the Tentelw Chemical Company.*

These processes, in their present shape, are the invention of Dr Georg Eschellmann, technical manager of the Tentelw Chemical Works at St Petersburg, and their chief engineer, Harmuth, and have been patented by them in common with the firm.

The following is a complete list of their patents, as supplied to me by the Company in 1911:—

### A. *Apparatus for making Sulphuric Anhydride by the Contact-process.*

Russia, 6691 and 6692 (1902), 10880 (1906), application 20th October 1909; Germany, 178762 (1904), 297095 (1909); Austria, 15751 (1903), 21164 (1905), 43754 (1910); Hungary, 26477 (1902), 32779 (1904), 49163 (1909); Italy, 139 (vol. 153), 189 (vol. 196), 314 (vol. 86); Switzerland, 26493, 32699, 49757; Great Britain, 11969 (1902), 20952 (1904), 23419 (1909);

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France, 321275 (1902), 3778 (addition to the above, 1904), 407914 (1909); Belgium, 163469 (1902), 179782 (1904), 219865 (1909); Sweden, 15967, 19742, 29437; Norway, 11372, 13975, 20029; United States, 792205 (1905), 937148; Roumania, 141, 1582; Spain, 46563 (1910); Japan, application 10th December 1909.

### B. Purification of Pyrites-burner Gases.

Russia, 8845 (1904), application 17th February 1910 (dust-chamber); Germany, 194176, 230585, application 18th January 1910 (dust-chamber); Austria, 32902 (1907); Hungary, 40648 (1907); Italy, 211 (vol. 268) of 1907; Great Britain, 12213 (1907); France, 379565 (1907); Belgium, 199923 (1907); Roumania, 685 (1907).

### C. Absorbing-tower.

Russia, 15586 (1909); Germany, 211999 (1907); Austria, 33808 (1908); Hungary, 41504 (1907); Italy, 187 (vol. 261); Switzerland, 41769 (1907); Great Britain, 22095 (1907); France, 382081 (1907); Roumania, 813 (1907).

### D. Apparatus for Cooling Hot Burner-gases.

Applications, September 1910 in Germany; June 1911 in Austria, France, Belgium, Switzerland, Sweden, Norway, Great Britain, Hungary, Spain, Russia.

The following statements on the Tentelew process have been supplied to me by the firm:—

*Cost of Plant.*—In St Petersburg 160,000 roubles, without the buildings and contact-mass, and without the apparatus for high-pressure air and for cooling purposes.

1. *Cost of the process* for one set, producing 300,000 pood<sup>1</sup> of acid, calculated as 94 per cent.  $H_2SO_4$ , *per annum*.

	Kopeks.*
Labour pro pood . . . . .	1.73
Carting pyrites to the burners . . . . .	0.16
Repairs and sundries . . . . .	2.00
Cooling-water . . . . .	(?)
Power (Diesel motor) . . . . .	...
Crude naphtha . . . . .	1.07
Total per pood 94 per cent. acid . . . . .	4.96 <i>without the cost of the pyrites.</i>

\* 100 kopeks = 1 silver rouble = Rs. 2.06d.

<sup>1</sup> A pood = 16.38 kg. = 36.112 lbs.

2. *Rate of Conversion.*—At least 95 per cent., usually 97 to 99 per cent., of the  $\text{SO}_2$  entering into the apparatus is converted into  $\text{SO}_3$ .

3. *Contact-mass.*—The same contact-mass has been in use in two apparatus for nine years, and still produces a conversion of 97 per cent.

4. *Sales.*—The process has been sold to Nobel Brothers at Baku (2 sets), Steaua Romana Company at Gampina (Roumania); Merrimac Chemical Company (at Boston, 2 sets); General Chemical Company, New York; Weiler-ter-Meer at Uerdingen (2 sets); Dynamite Nobel at Hamburg (3 sets); Dynamite Trust in London; Kopparbergs A. B., at Falun; Oehlich & Company at Riga; Uschkoff & Company at Kasan. (At the end of 1911, according to *Chem. Zeit.*, 1912, p. 218, 24 sets of the Tentelaw apparatus for 4000 tons  $\text{SO}_3$  each were at work in Russia, Germany, Roumania, Sweden, America, and Japan.)

5. *Quality of Product.*—Acid up to 100 per cent.  $\text{H}_2\text{SO}_4$  and fuming acid up to 30 per cent.  $\text{SO}_3$  are directly produced. Higher grades up to 100 per cent.  $\text{SO}_3$  can also be made, but not directly, as they solidify too easily. By simply turning a valve, without extra expense, either ordinary or fuming acid can be made. The acids are as clear as water and perfectly pure.

6. *Consumption of Pyrites.*—Theoretically each pood  $\text{SO}_3$  (100 per cent.) requires 0.8 pood pyrites (50 per cent. S). Practically the average consumption is 0.865 pood, equal to 0.67 pood 50 per cent. S per pood of 94 per cent.  $\text{H}_2\text{SO}_4$ . This supposes the plant to be properly conducted, so as to avoid mechanical losses, and the pyrites to be burnt down to 0.8 per cent. S.

Up to 1886 all the sulphuric anhydride consumed in the manufacture of lubricating oils from Russian crude naphtha had to be imported from abroad, at an abnormally high price paid to the Bohemian firm of Johann David Starck. In that year commenced the endeavours of the Tentelaw Company, which have led to a vast extension of that purely national Russian industry, by gradually lowering the price of sulphur trioxide through their systematic progress in that field. This required extensive studies and experiments, replacing one apparatus by

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another as experience was gained, and the Company had to try in the course of years many processes on a large scale before it finally succeeded in an economical working of the contact-process. Many hundreds of thousands of roubles were expended for this purpose, but in the end perfect success was obtained and acknowledged in 1896 by the grant of the Russian Eagle at the Nishni-Novgorod Exhibition. In December 1886 the first monohydrate was sold at R. 1.65 per pood, and the first fuming acid (15 per cent.  $\text{SO}_3$ ) at R. 3.25 per pood. At this day (July 1911) the price of monohydrate at the factory is only R. 0.72, that of 10 per cent. oleum R. 0.89, of 20 per cent. oleum R. 0.91, although in the meantime the purchasing-power of the rouble has been greatly lowered. Long before the respective patents of their competitors made their inventions known to the world, the Tentelew Company in 1894 employed their process for purifying the burner-gases, in 1889 the arrangement of the contact-mass in layers and perpendicular contact-pipes, in 1891 a multiplicity of contact-pipes, etc., etc. In 1901 the Company resolved to protect their processes by patents in most countries; their applications were strongly contested, first in Germany, then in England, but the opposition was defeated.

During the first years it was merely a question of cheapening the manufacture of the fuming O.V., but later on, when some of their competitors, in the first line the Badische Soda- und Anilinfabrik, had most successfully carried through the entire abolition of the chamber-process in favour of the contact-process, the Tentelew Company had equally to approach the manufacture of ordinary sulphuric acid by that process. In this endeavour they ultimately succeeded so completely that the Badische Company, after having convinced themselves of that success, agreed with the Tentelew Company to proceed in future in common and to exchange their experiences. The Tentelew Company has gradually taken down all their chambers and now works with five contact-systems, which occupy very much less space.

From the following description the differences between the Tentelew and the Badische process are clearly visible.

Concerning the *purification* of the burner-gases, the German Patent Office on 5th November 1905 decided that the Tentelew

process, for which a patent had been applied on 23rd May 1901, was the result of original inventive action, and on 16th March 1907 the patent was granted, against the opposition of the Badische on the strength of their Ger. P. 113933 and B. P. 15948 of 1898, and of various other previous publications. It was specially acknowledged that valuable advantages are attained by the *successive* removal of sulphuric acid and chlorine from the burner-gases, especially a small consumption of alkali for retaining the chlorine, obtention of the sulphuric-acid fog in a valuable form, avoidance of an obstruction of the washing-apparatus. The following table explains the differences in the purifying operations of both companies:—

<i>Badische.</i>	<i>Tentelw.</i>
1. Addition of aqueous vapour to the hot burner-gases.	1. No such addition is made.
2. Cooling.	2. Cooling.
3. No filtration.	3. Dry filtration and separation of sulphuric-acid fog.
4. Washing with sulphuric acid for the purpose of removing the sulphuric-acid fog.	4. No such operation.
5. No treatment with alkali.	5. Washing with alkaline liquor.

The Tentelw purifying process is characterised by dry filtration and separation of the fog before washing, and by the application of *alkali* for purifying the gases, thus introducing a chemical purification, whereas the Badische process of purifying by means of sulphuric acid employs mechanical and physical means. The great advantage of the Tentelw process is proved by the fact that the same contact-mass has been working in their first large contact-apparatus during the last nine years, and still yields a 97 per cent. conversion of  $\text{SO}_2$  into  $\text{SO}_3$ . Their Ger. P. 230585 describes a new kind of washing the gas-filters.

The *contact-apparatus* of the Tentelw Company is specially characterised: (1) By a large empty vessel, placed in front of the contact-mass, which acts as a cooler of the gases by radiation; (2) By a peculiar combination of the contact apparatus with a regulator. In the empty vessel No. 1 the excess of heat of reaction of the contact-mass is transferred to the entering cooler gases by radiation, not by a counter-current, an exact



regulation of the temperature being effected, by the regulator No. 2. By this direct exchange of heat, any injurious overheating of the contact-mass is completely excluded; practice has shown that the above combination suffices for working and regulating the apparatus *without applying any other heat* than that produced by the contact-mass itself, and that no injurious overheating of that mass takes place. As is well known, most of the heat is produced at the place where the  $\text{SO}_2$  gases first come into contact with the contact-mass; in the Tentelew apparatus just that place is most strongly cooled by radiation into the preceding empty vessel. The lower portions of the contact-apparatus require no further cooling, and do not get it, as most of the  $\text{SO}_2$  is already higher up oxidised to  $\text{SO}_3$ , and further cooling would be even prejudicial for attaining a conversion of 97 or 98 per cent. This process differs very much from the Badische, which cools the pipes of their apparatus from the outside, all along their length, by means of cold  $\text{SO}_2$  gas entering principally at the bottom. In the Tentelew apparatus the gases enter only in one place at the top and go away at the bottom. The lower portion of the contact-mass is also working very nearly at the optimum of temperature for reacting, which is very important in view of the enormous rise of the price of platinum.

A second very important and characteristic part of the contact-apparatus is the *regulator*. This apparatus effects, firstly, the regulation of the temperature inside the contact-apparatus; secondly, a first, but only partial, preheating of the cold  $\text{SO}_2$  gases before entering into the top of the contact-apparatus; thirdly, the contemporaneous cooling of the very hot  $\text{SO}_3$  gases issuing from the apparatus. This first cooling admits of applying quite a small air-cooling apparatus for the further cooling of the  $\text{SO}_3$  gases. The regulation of the temperature is effected according to the principle of counter-currents, by compelling a portion of the hot  $\text{SO}_3$  gases, which can be regulated at will, to pass through the regulator in counter-current to the cold  $\text{SO}_2$  gases and yielding up heat to these. This apparatus has been a complete success, and works with astonishing rapidity and regularity.

The principle of counter-currents was first introduced in the contact-process by the Farbwerke Höchst, in their Ger. P. 105876 of 6th January 1898, and 109483 of 17th May 1898. They apply

it for transferring the excess of heat of the  $\text{SO}_3$  gases upon the entering cold  $\text{SO}_2$  gases *in order to produce the temperature requisite for the reaction*, in case of need with introduction of superheated aqueous vapour to the  $\text{SO}_3$  gases passing out. The Badische also applies counter-currents for heating up the entering  $\text{SO}_2$  gases by the  $\text{SO}_3$  gases flowing in the opposite direction in the contact-apparatus; this takes place not outside, but inside the contact-apparatus, and not merely for heating-up the  $\text{SO}_2$  gas, but principally for cooling the contact-mass in a way easy to regulate, and in specially constructed apparatus, with special arrangements for regulating the temperature, both inside and outside the contact-apparatus. The Tentelw Company effects the three functions of regulating the temperature of the contact-apparatus, partial heating-up of the  $\text{SO}_2$  gases and cooling of the hot  $\text{SO}_3$  gases in a specially constructed regulator.

The Tentelw Company claims to convert the greatest possible quantity of  $\text{SO}_2$  into  $\text{SO}_3$  by the least possible quantity of platinum, with a minimum of attendance, without any expenditure of fuel, in case of proper attendance upon the purifying-apparatus also without any disturbance, with a perfectly regular conversion of the  $\text{SO}_2$ , and without any change of the contact-mass. Their apparatus lasts for an indefinite period. All parts of it have been in uninterrupted work for nine years past; only the cooler for the burner-gas has been replaced by a new apparatus, for which patents have been applied, and which finally solves the difficult problem of suddenly cooling red-hot burner-gas, charged with flue-dust and sulphuric-acid vapours, down to below  $100^\circ$ , without interrupting the work and with easy removal of the mud and the condensed sulphuric acid, with the certainty of lasting for many years.

The *absorption* of the  $\text{SO}_3$  formed in the contact-apparatus, and cooled first by the regulator and then by a small air-cooler, is performed in a patented absorbing-tower, the efficiency of which has been proved by many years' function. It completely retains the  $\text{SO}_3$  and produces at will fuming acid up to 30 per cent.  $\text{SO}_3$ , or monohydrate, or acid of  $66^\circ$  B $\acute{e}$ , all of them perfectly clear. The work is very simple; the  $\text{SO}_3$  gases enter at the bottom, in counter-current against the absorbing-acid flowing in at the top. The tower is of no great height, takes

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very little space, and is much cheaper than the absorbing-apparatus hitherto employed.

The following abstracts from the various patents of the Tentelw Company give a clear idea of the apparatus and process, as far as they go. Beyond this perfect secrecy is kept, especially with regard to the preparation of the contact-mass, which is of great importance, and has made it specially possible to work with much less motive power than before for propelling the gases, by lessening the frictional resistance of the mass within the contact-apparatus.

In conclusion, it is stated in the communication made to me that the most energetic initiative for taking up the contact-process in 1886 is due to the then general manager, Dr W. von Schneider, most efficiently seconded by Dr Georg Wischin up to 1898, when he was succeeded by Dr G. Eschellmann, who brought the processes to their present state, with the assistance of chief-engineer Harmuth, by ten years' self-sacrificing devotion.

### *Patents of the Tentelw Chemical Company.*

1. *For Purifying the Pyrites-burner Gases from Chlorine.* (Ger. P. 194176; B. P. 12213 of 1907, etc.)

To begin with, the fog of sulphuric hydrate is thoroughly removed by filtering the gases through coke, and then the gas is washed with an aqueous solution of hydrates of alkalis or alkaline earths. This is far preferable to the process described in B. P. 15948 of 1898, according to which the gases are treated while hot with steam, cooled down and washed with water, to which sodium bisulphite or similar chemicals have been added, for the present invention confines the action of the alkali entirely to absorbing the chlorine. For this purpose the gases are first passed through a dust-chamber, provided with shelves, in which the coarser particles of the dust are retained and the sulphur is completely burned. They now pass into a space cooled by water, where more dust is retained in the shape of soft mud, and much of the sulphuric-acid fog is condensed to acid of about 52° Bé., which runs away continuously. In order to remove the finest dust and the last portions of the sulphuric-acid fog, the gas now passes from the bottom upwards through a large coke-filter, built up of particles of coke, diminishing

from the bottom upwards, finally to about 10 mm. diameter. In this "coarse filter" most of the acid is condensed to acid of  $40^{\circ}$  B $\acute{e}$ , and it retains both mud and dust carried over. This filter can be easily cleaned from dust, etc., by means of water forced upwards in brick channels, on which the coke is resting. Two such "coarse filters" are provided, one of which is at work while the other one is being cleaned out. The gas now enters the "fine filters," of which there are also two provided, one of which only is at work. These are charged with coke down to a grain of only 1 mm. Here the finest dust and fog is retained. The gas enters from the top, so that the dust deposits there; this is essential, the cleaning being effected by taking out the top layer of coke, as far as it is soaked with dust, and replacing it by fresh coke, whereupon the filter is at once ready for use again. This is necessary only once *per annum*, and such filters can go on working for years without refilling, whilst they would be quickly useless if the mud were removed by washing. Just on this account it is most essential that the gases should enter into this "fine-filter" from the top. The gases are now passed through a series of washers, filled with an aqueous solution of an alkali or a milk of an alkaline earth hydrate, preferably milk of lime. Here the corresponding bisulphites are formed which enter into reaction with the chlorine contained in the gas. Any traces of sulphuric acid still present are retained in the shape of calcium sulphate. The gas comes out absolutely free from chlorine; it is dried and then passed into the contact-apparatus.

Eschellmann and the Tentelewsche Chemische Fabrik (B. P. 12213 of 1907; Amer. P. 900500) pass the gases through a dust-chamber, then to a cooling apparatus, where the condensing liquid is run off, then upwards through a filter, consisting of coke grains decreasing in size from bottom to top, and at last through a fine grained coke filter in a downward direction; they are then washed with weak lime water and dried in the usual manner. Cf. also B. Ps. 15948 of 1898 and 3327 of 1901.

The Tentelew Chemical Company (Ger. P. 23585) improve their filter by a special arrangement for washing out the impurities.

Eschellmann and Harmuth (Amer. Ps. 937147 and 937148) purify the gases used in making  $\text{SO}_3$  by the contact-process from

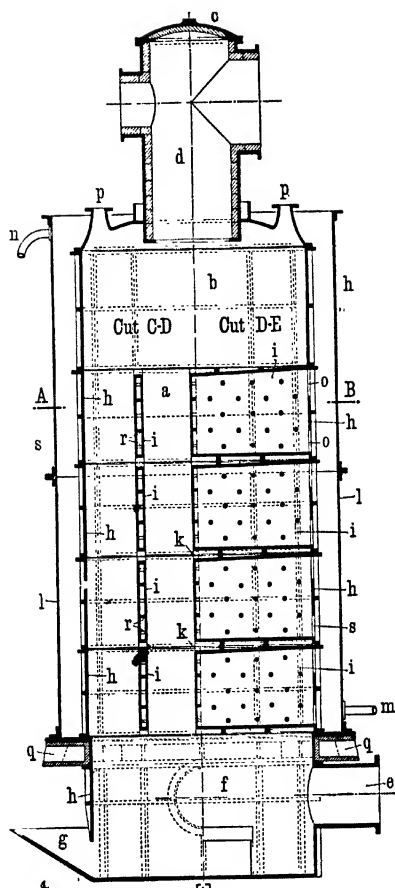


FIG. 497.

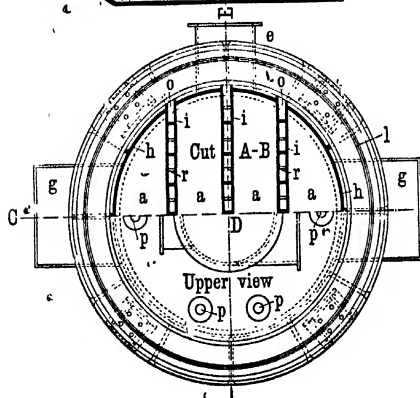


FIG. 498.

lubricating-oil, taken up from the gas-pumps, by filtration through coke.

2. *For Cooling the Hot Burner-gases.* (Patent applications made in Germany in September 1910 and in other countries in June 1911.)

This cooling is a difficult task. The direct cooling by flushing with sulphuric acid has had to be abandoned, on account of the expense of pumping and the quick contamination of the acid. The indirect cooling of the gases, which are at about  $500^{\circ}$ , by means of leaden tubular coolers is awkward on account of the rapid destruction of the tubes by hot sulphuric acid and crusts of flue-dust, and the difficulty of cleaning them. These drawbacks are avoided by applying hollow plates, through which the cooling-agent is flowing, as shown in Figs. 497 and 498.

Fig. 497 on the left side gives a perpendicular section through C—D of Fig. 498, and on the right side through D—E of Fig. 498. Fig. 498 is a horizontal section through A—B of Fig. 497.

The apparatus consists of a cylindrical cooling-chamber *a*, a preliminary chamber *b* into which the gases enter at the top through the pipe *d*, provided with a cover *c*, and a collecting-chamber *f*, open at the bottom, with an outlet *e* for the cooled gases and dipping into a trough *g*, where the collecting acid furnishes a hydraulic seal for the cooler. This chamber *f* is built up of a number of rings *h*, the flanges of which are soldered together, each of which rings contains several (in our drawing three) hollow plates *i*, *i*. These plates do not quite reach to the top of the ring, and they are kept in their places by the stays, *k*, *k*. Chambers *a* and *b* are surrounded by an outer mantle *l*, which at the bottom is provided with a conduit *m* for cooling-water, and at the top with an outlet *n* for the same. The cooling-plates *i*, *i* communicate with *l* at the top and bottom by rows of slits, *o*, *o*. The top side of the cooling-plates is inclined from inside to outside.

The preliminary chamber *b* and the collecting-chamber *f* are also built up of rings, *h*; on chamber *b* a number of branch-pipes *p*, *p* are arranged as inlets for the water. The mantle *l* is made of wrought-iron, all the other parts of pure cast-lead, and the whole rests upon a cast-iron ring *q*. The cooling-plates

are stiffened by numerous cross stays *r* and the rings *h* by ribs *s*.

The hot gases are passed into *d*, fill the chamber *b*, and are divided in this on the interstices between the cooling-plates *i*, along which they flow below into the collecting-chamber *f*, and issue through *e*. The cooling-water enters at the bottom through pipe *m* into the mantle *l*, rises in this and through the cooling-plates *i* and flows out at *n*. Any bubbles of air given off from the water pass under the outwardly rising top plates into the mantle. The condensed sulphuric-acid drops fall into the trough *g*, and freely run away here.

For rinsing the cooler, water is let in by the top necks *p*, and gets out with the mud washed away from the cooling-plates, into trough *g*.

The gases, entering at a temperature of 500°, are cooled down to ordinary temperature by a single passage through the apparatus. By this rapid cooling the sulphuric acid present is very completely removed. No mud adheres to the cooling-plates, which are washed once in from four to six weeks; there is no danger of stopping up. The cooler is easily accessible for repairs by taking away the cover *c* through *d*.

3. *Contact-apparatus*.—In their B. P. 11969 of 1902, the Tentelw Company described a tubular contact-apparatus, protected against overheating by arranging a preliminary equalising empty space into which the gases, after being duly preheated according to the indications of a thermometer placed in the zone of the strongest reaction, are passed from above, and into which the upper ends of the tubes radiate a considerable portion of the heat, developed in the tubes. After recognising that the strongest reaction and the greatest development of heat takes place in the upper portion of the contact-tubes, and but little conversion, and consequent development of heat takes place in the lower portion, the Company, according to their B. P. 20952 of 1904; Ger. P. 178762, etc., etc., made the following arrangements. The principal portion of the contact-mass is placed on a sieve-plate, forming the bottom of the equalising space, in a uniform layer, and the remainder of the contact-mass in a space below this, not connected with the equalising-space, and carefully protected against loss of heat. Since the upper portion of the contact-mass, which comes into contact with the

fresh gases, presents a great surface, it can radiate a great deal of heat into the empty space and is thus prevented from getting overheated. Since, moreover, the fresh gases are preheated by the anhydride vapours outside the apparatus only so far that, on passing through the equalising-space, their temperature does not exceed  $450^{\circ}$  (as shown by a thermometer placed at the surface of the contact-mass), that is, the best temperature for the conversion of  $\text{SO}_2$  into  $\text{SO}_3$ , the principal portion of the  $\text{SO}_2$ , say 90 to 95 per cent., is thus converted in the upper layer of contact-mass, and the remainder, up to 97 or 99 per cent., easily and quickly in the lower reaction space, where consequently but little heat is developed, so that this space must be carefully protected against cooling by means of a heat-retaining covering. The spreading of much of the contact-mass on a large surface also leads to a saving of about half of the power, required for propelling the gases, in comparison with the older tube apparatus; moreover, the apparatus is cheaper and the sieve-plate can be made of cast-iron. The apparatus is easily heated up, and then works without any expenditure of fuel.

A further improvement was effected by an arrangement protected by B. P. 23419 of 1909; Ger. P. 227095; Amer. P. 937148 of Eschellman, Harmuth, and the Tentelw Chemical Company. Here the sieve, bearing the principal layer of the contact-mass, is so constructed as to be easily taken out in pieces, each of them provided with a vertical pipe projecting above the contact-mass, for the purpose of separate cleaning-out, and the equalising-space is surrounded by a permanent hot layer of gas.

This arrangement is shown in Fig. 499, giving a perpendicular section, and Fig. 500 a horizontal section through the right-side half on the line q—q of Fig. 499. The cylindrical chamber A, forming the "equalising-space," has a cover E with gas-inlet H. The smaller lower chamber C is connected with it by the conical space B; a thorough mixture of the gases is effected by the plate P, with central opening *a*. Similarly the sieve-plate J, composed of several pieces (to be taken out separately for cleaning), serves for mixing and equally spreading the gases entering through H. Below this sieve-plate there is a conical piece K, tightly joined to the side of A, and closed at



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the bottom by a flange *h*, on which rests the sieve *L*, which is moreover supported from below by the rings *i'*, *i*<sup>1</sup>, and the pillars *j*. On the sieve *L* is placed another sieve, composed of a number of perforated square plates *m*, *m*, each of them surmounted by the pyramides *M*, which are open at top and bottom. The principal portion of the contact-mass, *c.g.* platinised asbestos, is spread on the plates *m*, *m*, in a layer reaching nearly to the top of the cones *M*, *M*. If the apparatus

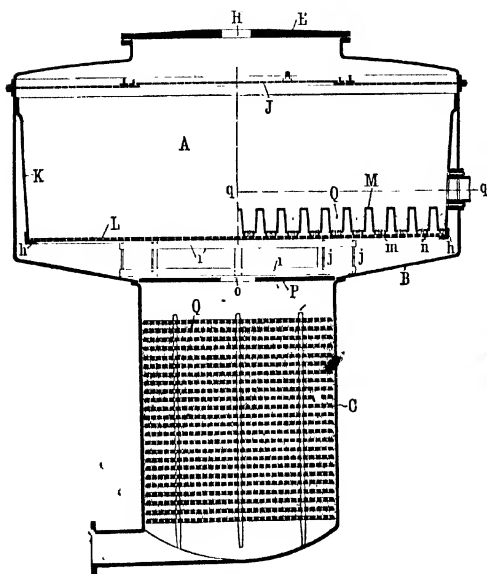


FIG. 499.

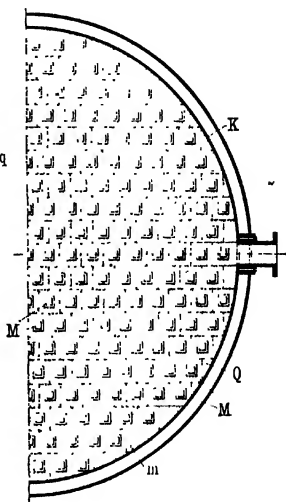


FIG. 500.

is to be stopped for replacing the contact-mass entirely or partially, the top plate *E* is removed, then the sieve-plate *J*, and now only one of the plates *m*, *M* can be taken out without disturbing the other plates. The cones *M*, *M* are of special value for the regulation of the temperature; they abstract heat from the contact-mass *Q*, and convey it by radiation to the gases above. The gases, on leaving the mass *Q*, also yield much of their heat to the plate *L*, which conducts it away through the cones *M*. Plate *L* is also best made in pieces to be taken out separately. By providing a conical empty space

round the cylindrical chamber A, which at the bottom is in connection with the mixing-chamber B, a stagnating layer of gas round K is created which greatly assists in protecting A against loss of heat by radiation, apart from the heat-insulating layer round that chamber, not shown in the drawing.

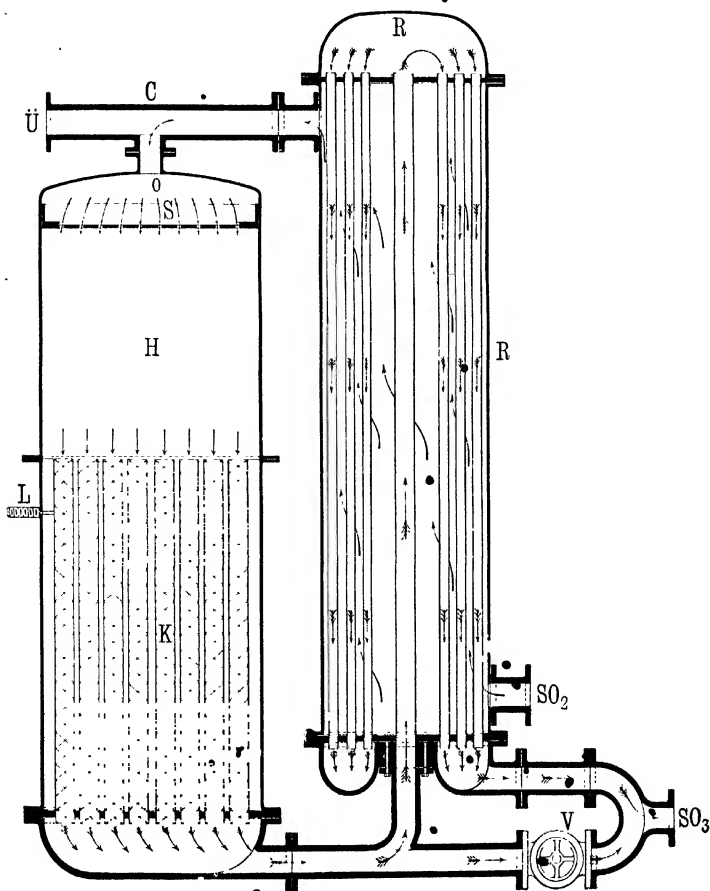


FIG. 501.

4. The "Regulator," mentioned *suprà*, p. 1362, is shown in Fig. 501, in connection with the tubular contact-apparatus.

The contact-mass is contained in the tubes K; H is the equalising space above them; S the sieve-plate on which rests the principal portion of the contact mass; L the thermometer; *o* the upper inlet of the gases; U the pipe leading to the super-heater, to be used only on starting the apparatus; C the connecting-pipe with the regulator; R the regulator, V the regulating-valve. The plain arrows show the course taken by the SO<sub>2</sub> gases from the pyrites-burners; the feathered arrows the course of the gases after the conversion into SO<sub>3</sub> has been effected.

5. The *absorbing-tower* (B. P. 22095 of 1907; Ger. Ps. 211999, etc.) is shown in Fig. 501 in vertical section and in Fig. 502, half as seen from the top and half in horizontal section. Three (or more) chambers, *a*, *a*<sup>1</sup>, *a*<sup>2</sup>, are superposed over one another. Each of them contains a specially shaped gas-entrance pipe *b*, surmounted by a dish *c*, which is tightly connected with the sides of the chambers, and provided with a perforated margin, *d*. The gases are thus compelled to spread equally over the horizontal section of the tower. Fig. 502 shows that the series of holes are arranged in alternate places, which causes a very intimate contact between the gas and the liquid, as the gas bubbles are thereby prevented from flowing together. This produces a very perfect absorption, and allows of correspondingly decreasing the height of the liquid and the resistance offered by it. Any carrying-away of liquid is also prevented by the way in which the holes of the zone *d* are arranged, so that the gas-bubbles are easily detached and any strong movement of the liquid is avoided. In order to promote the absorption, the space near that perforated zone is efficiently cooled, by surrounding the chamber with a cooling-mantle, *e*, and arranging the perforated zone, in such an angle to the chamber-sides that the liquid is thrown against these cooled sides in the direction of the arrows. In the top-chamber the pipe *b* projects higher up from the liquid than in the lower chambers, so as to facilitate the absorption of the last portions of the gas. The finer the holes in the zones *b*, the better is the division of the gases, and the quicker the absorption. The clear space of the holes is best made *in summa* equal to the exit opening of the pipes *b*. The sulphuric acid, serving for absorbing the gas, is either introduced near the top at *f* and flows

FIG. 502.

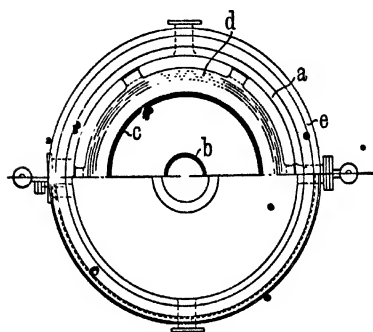
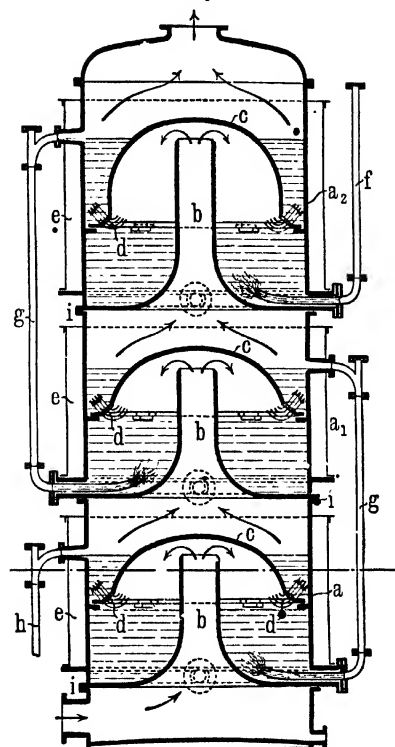


FIG. 503.

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through all the chambers by means of the connecting-pipes *g*, ultimately running-out at *h*, or each chamber is provided with a separate inlet and outlet for the acid. The last-mentioned arrangement allows of preparing acids of various percentages; in the first arrangement the percentage of the acid running away through *h* is regulated by the acid introduced at *f*. Care is taken to prevent the joints at *i*, where the chambers are connected, from any contact with acid.

#### III. *Process of the Farbwerke, vormals Meister, Lucius, & Brünig, at Höchst.*

This process has been worked out by Dr C. Krauss and is described below by himself. Patents: B. P. 6057 of 11th March 1898; 14728 of 4th July 1898; 285 of 5th January 1899; 1385 of 21st January 1901; 2368 of 4th February 1901; 3161 of 7th February 1902; 4026 of 17th February 1902; Amer. P. (Krauss and von Berneck) 702512 of 26th May 1902; Ger. Ps. 135887, 139554, 169728.

The following communication has been made to me by the above firm. It is penned by Dr C. Krauss, the real inventor of the processes in question, and Dr Rudolph Müller von Berneck:—

The Höchst Farbwerke, one of the first firms which have made sulphuric anhydride on a large scale by the contact-process, at first employed the process of Winkler, by decomposing concentrated sulphuric acid at a high temperature into  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ , removing the latter and passing the  $\text{SO}_2 + \text{O}_2$  over platinum asbestos. Attempts were made many years ago to convert purified pyrites-kiln gases into  $\text{SO}_3$ , but not with technically satisfactory success. Therefore extended experiments were made, both on a large scale and in the laboratory, with pure liquid sulphur dioxide and dry air, afterwards with gases produced by burning sulphur in air, which led to the result that a satisfactory yield of  $\text{SO}_3$  from  $\text{SO}_2$  was easily attained by keeping the reaction within definite limits of temperature. George Lunge has the merit of having first made this observation, and having first publicly expressed it. In his B. P. 3566 of 1888, taken for him by Ellice Clark, he says, verbatim:—“The temperature in that part of

the apparatus where the combination of  $\text{SO}_2$  and  $\text{O}_2$  takes place must be carefully regulated, and must be neither too high nor too low (preferably at or below a dull red-heat)."<sup>1</sup>

On the strength of their observations and trials, and on the strength of the fundamental discovery of Lunge, the Farbwerte erected a plant for making  $\text{SO}_3$  from pyrites-kiln gases for a daily consumption of 15 tons pyrites. The gases were first freed from all impurities by washing with steam, water, and a solution of bisulphate (for the removal of fluorine and chlorine compounds), and drying by sulphuric monohydrate in specially constructed apparatus. They were then passed into the contact-furnace, Fig. 504. Here they were heated in the pipes HH, and subjected to catalysis in the two contact-retorts  $C_1$  and  $C_2$ . Retort  $C_1$  was placed within the furnace above the fire-grate F, retort  $C_2$  outside the furnace. The gaseous current and the fire were regulated in such manner that the gases issuing from retort  $C_2$  at A showed a temperature of  $400^\circ$  to  $450^\circ$  C. The gases were then cooled, and the  $\text{SO}_3$  absorbed by concentrated sulphuric acid in cast-iron absorbers placed terrace-wise, so that ordinary acid was run in at the top, and fuming acid run off at the bottom. The gases were compelled to bubble through the acid in each absorber; these were cooled from the outside by flowing water.

This plant worked satisfactorily for many years; but soon the idea arose of gaining the considerable amount of heat required for heating the gases from one of the sources of heat offered by the process itself. As the most convenient of these was chosen the heat stored up in the gases issuing after the reaction from the contact-retorts.

The result of this work was the Ger. P. 105876 and B. P. 6057 of 1898, in which is claimed "the method of raising the gases to the temperature required for the reaction, by transferring to them heat from the produced sulphur trioxide." The transference is effected by a simple counter-current apparatus.

The working out of this process on the large scale commenced with great difficulties. Chiefly in consequence of the large dimensions of the apparatus, it was not easy to keep the

<sup>1</sup> I do not myself claim priority in this respect. Long before the above patent it had been pointed out that the temperature of the contact-oven must be regulated as above; cf. also *supra*, p. 1352.—G. L.

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temperature within the limits most favourable for the production of  $\text{SO}_3$ . This was remedied by Ger. P. 119505 (B. P. 285 of 1899). Here the temperature of the contact-space is

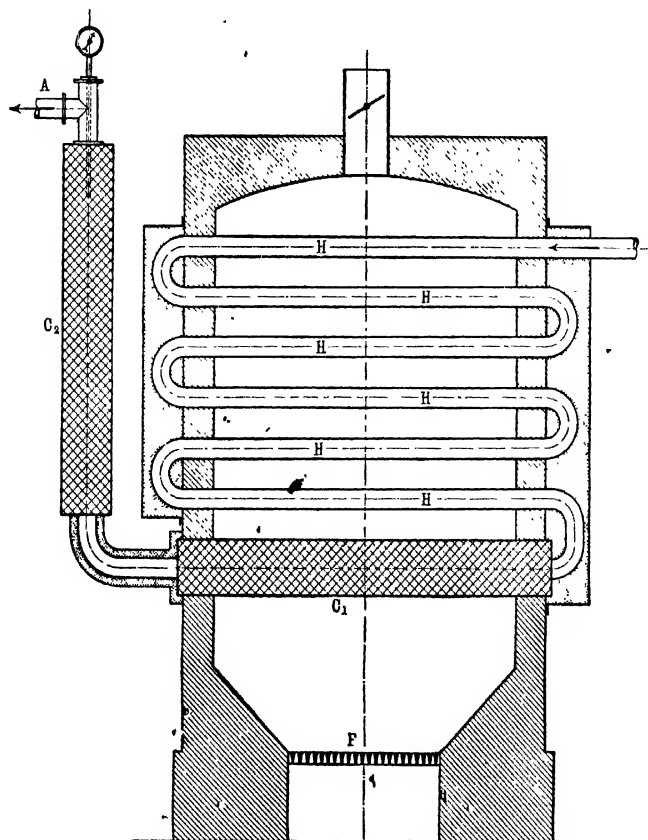


FIG. 504.

regulated by mixing the reaction-gases overheated therein with cold  $\text{SO}_2$  gases, and thereby lowering the temperature for the time being.

In connection with the above work, investigations were made respecting the influence of the compression of roasting-

gases on the formation of  $\text{SO}_3$ . Schröder and Hänisch (Ger. P. 42215) had proposed to work at a pressure of 2 or 3 atm. above the ordinary pressure. Our investigations showed, as is distinctly stated in the first of the above-mentioned patents, that "the reaction goes on at any pressure, but best quantitatively at a plus-pressure." But they further showed that the advantage produced by artificial high pressure in slightly altering the chemical equilibrium in favour of the formation of  $\text{SO}_3$  is not at all equivalent to the increased consumption of steam required for that high pressure. Our efforts were therefore from the first directed towards reducing the inner resistance of the apparatus, in order to reduce the expenses for steam.

Pressure certainly plays an important part in the reaction, as is proved by theoretical reasoning instituted by Professor Bredig, with the result that under certain circumstances pressure exercises a considerable effect on the equilibrium  $(2\text{SO}_2 + \text{O}_2) + x \rightleftharpoons 2\text{SO}_3$ ; but with the pressures possible in technical operations that influence is very slight, and the advantage gained thereby does not correspond to the increased expense for motive power.

A knowledge of the equilibrium-constants was very valuable, by presenting a security for attaining the equilibrium as soon as the constant calculated from the analytical data shows the proper value for the temperature in question. If the constants are known for one or several temperatures, the value of  $K$  can be calculated for any other temperature by means of the reaction-heat.

The constants were determined as follows.—Tubes of Jena high-pressure glass holding 20 c.c. were drawn into capillaries at both ends, and charged with about 5 g.  $\text{SO}_3$ . One of the capillaries was sealed, and the air pumped out as well as possible. This is more easily performed if the  $\text{SO}_3$  is heated to boiling, its heavy vapours driving out the air. When about nine-tenths of the  $\text{SO}_3$  had been evaporated, the second capillary was sealed as well. The tubes, which contained about 1 m. of platinum wire as a catalyst, were heated during three or four days in a thermostat to the required temperature. Without platinum wire the reaction was so slow that the equilibrium was not reached even after heating for weeks.



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The temperatures ranged between  $465^{\circ}$  and  $515^{\circ}$  C. At lower temperatures the velocity of reaction was too small, at higher temperatures the glass became soft and the tubes were blown out. After the equilibrium was attained, the contents of the tubes were analysed, and the constants calculated therefrom. This requires knowing the concentrations of  $\text{SO}_3$ ,  $\text{SO}_2$ , and  $\text{O}$ ; but as it is very difficult to estimate all three, only  $\text{SO}_3$  and  $\text{SO}_2$  were estimated; the concentration of  $\text{SO}_2$  must be proportional to that of  $\text{O}_2$ . The formula

$$\frac{(\text{C} \cdot \text{SO}_3)^2}{(\text{C} \cdot \text{SO}_2)^2 + \text{C} \cdot \text{O}} = K$$

must then be changed into

$$\frac{(\text{C} \cdot \text{SO}_3)^2}{(\text{C} \cdot \text{SO}_2)^2} = K.$$

This formula was applied to the calculation of the constants. The single values thus found did not agree very well, because the dust absorbed some oxygen, and the glass tubes are to some extent acted upon; in a few cases even the platinum wire showed some action by a bluish-black colour, which vanished when igniting the wire in the air, and therefore probably consisted of a platinum oxide.

The following average values for  $K$  were obtained from fourteen (respectively twelve) experiments:—

At $515^{\circ}$ C.	At $465^{\circ}$ C.
18,590,000	83,618,000

The volume of the tubes was expressed in litres.

To check these values, other similar tubes were charged with a mixture of  $2\text{SO}_2 + \text{O}_2$ , and heated till the equilibrium was attained. The results agreed with those previously found in the order of magnitudes.

If we insert these equilibrium-constants in the formula expressing the proportion of reaction-heats to equilibrium-constants (Nernst, *Theor. Chem.* p. 599), we find the reaction-heat  $Q$ , if  $K_1$  is the equilibrium-constant at  $T_1$ ,  $K_2$  the same at  $T_2$ :

$$Q = \frac{4.584 (\log K_2 - \log K_1) T_1 T_2}{T_2 - T_1} \text{ calories,}$$

$$Q = \frac{4.584 (\log 83,618,000 - \log 18,590,000) 787.737}{50}$$

$$= 34,670 \text{ calories.}$$

hence  $(\text{SO}_2, \text{O}) = 17.3$  calories, whereas Thomson gives 20.5 and Berthelot 22.6 calories (Ostwald, *Lehrb.*, ii. 1, pp. 123, 124).

After, in the above-described way, the very considerable expense for the direct heating of the gases in the contact-process had been eliminated, and the cost of motive-power for high pressure had been reduced, efforts were made for saving as much as possible of the power for propelling the immense volume of gases through the apparatus. Chimney-draught appeared insufficient, on account of the considerable inner

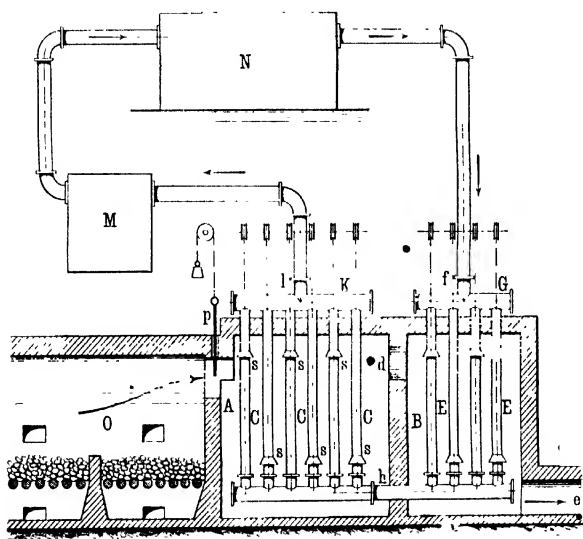


FIG. 505.

resistance, especially in the apparatus for purifying the gases and absorbing the  $\text{SO}_2$ . Hence steam had to be retained as the source of motive-power, and attempts were made to cheapen its production by utilising the combustion-heat of pyrites. This was done in the way shown in Fig. 505. The gases leave the pyrites-kiln O with a temperature of  $600^\circ$  or  $700^\circ$  C., and enter a chamber divided by a partition into two parts, A and B. In A they play round iron pipes C, provided with movable scrapers s, and yield up part of their heat to the water circulating therein, thereby producing some steam. They now

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pass through *d* into the second chamber B, and again play round pipes E, provided with scrapers and connected with pipes C C. In E the gases yield up their remaining heat. The water travels in the opposite direction to the gases, entering at *f* and leaving the pipes at K in a heated state. The steam thus generated issues at *l*, passes into the heat-regulator M, and from there with as uniform a temperature as possible into the "cold-steam engine" N, from which the condensing water flows back to G. These experiments are not yet brought to a satisfactory issue.

In connection with these technical experiments, exhaustive laboratory researches were made on the catalytic process, which are still partially in progress.

Since in the reaction  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ , the concentration of two substances is changed, that reaction, according to our present views, ought to be of the second or third order. But since in technical kiln-gas, containing 6 or 7 vol. per cent.  $\text{SO}_2$ , there is a very considerable excess of oxygen, practically only the concentration of  $\text{SO}_2$  will alter to a considerable extent, and the process will go on approximately as a reaction of the first order, *i.e.*, the quantity transformed in the unit of time will be directly proportionate to the concentration of  $\text{SO}_2$ .

If we denote by 1 the time required for transforming the first 10 per cent.  $\text{SO}_2$  of that present in the kiln-gases into  $\text{SO}_3$ , during the time 2, from the residual gases, now containing only 90 per cent. of the original  $\text{SO}_2$ , not 10 per cent., but only 9 per cent. will be transformed. In order to catalyse the whole of the 10 per cent., we must employ 10/9 units of time, and so forth, so that we obtain the following series:—

Per cent. $\text{SO}_2$ .	Units of time = Units of Catalysis.
100 to 90	$10/10 = 1$
90 „ 80	$10/9 = 1.11$
80 „ 70	$10/8 = 1.25$
70 „ 60	$10/7 = 1.43$
60 „ 50	$10/6 = 1.67$
50 „ 40	$10/5 = 2.00$
40 „ 30	$10/4 = 2.50$
30 „ 20	$10/3 = 3.33$
20 „ 10	$10/2 = 5$
10 „ 0	$10/1 = 10$

14.3

15

When working with a continuous stream of gases, "time" means the time of contact with the catalyser, and "unit of time" the unit of catalysis required for transforming the first 10 per cent.  $\text{SO}_2$ . We then see that the first 80 per cent.  $\text{SO}_2$  is transformed into  $\text{SO}_3$  in about the same time or by the same quantity of catalyser as is required for the transformation of the last 20 per cent.  $\text{SO}_2$ , assuming the temperatures to be equal.

In every chemical reaction, whether endothermic or exothermic, the velocity of reaction and the finally attained equilibrium depend on the temperature, or in other words, under otherwise equal conditions, there belongs to each temperature a certain velocity of reaction and a certain equilibrium. We know that the velocity of reaction increases with the temperature, and thermodynamics teaches us that the equilibrium with the rise of temperature changes in that sense that those products increase which are formed with absorption of heat. Formerly nothing was found in literature concerning the temperature within the contact-space except the uncertain expression of "a red heat." The above-mentioned British patent of Lunge's for the first time contains the demand that the temperature within the contact-space must be carefully regulated. This idea was taken up by the Höchst Farbwerte in their B. P. 285 of 1899. But the aim of thorough rational work was not yet reached in that way, viz., to combine the largest possible velocity of reaction (the smallest possible amount of contact-substance) with the largest possible yield of  $\text{SO}_3$ . This was not easily attained in the manner previously followed. We may certainly increase at will the velocity of reaction by raising the temperature, but at the same time we change the equilibrium between  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_3$ . This is distinctly proved by experiment. At  $408^\circ$  the reaction was almost quantitative, at  $500^\circ$  only 90 per cent., at  $530^\circ$  only 80 per cent. of the  $\text{SO}_2$  is transformed into  $\text{SO}_3$ .

A further result of the research was the surprising increase of the velocity of reaction with the rise of temperature. With finely divided platinum as a catalyser, it is sixty or eighty times as great at  $500^\circ$  as at  $400^\circ$ , and increases still further at higher temperatures. We find that the same contact-mass

## 1382 MANUFACTURE OF FUMING OIL OF VITRIOL

which at  $400^{\circ}$  transforms 100 parts  $\text{SO}_2$  into  $\text{SO}_3$ , at  $520^{\circ}$  transforms  $80 \times 80 = 6400$  parts  $\text{SO}_2$  into  $\text{SO}_3$ , and the proportion is still better at higher temperatures.

From these experimental results we conclude *that really great velocities of reaction, even when employing excellent catalysers like finely-divided platinum, occur only at such temperatures at which the percentage yield of  $\text{SO}_3$  begins to be inferior, and that a combination of both advantages is not possible so long as the whole contact-space is kept at a uniform temperature such as had hitherto been aimed at.*

Hence experiments were made for conducting the catalytic process within the contact-space at varying temperatures, viz. keeping the temperature in the first zone of reaction high enough for oxidising most of the  $\text{SO}_2$  into  $\text{SO}_3$ , and afterwards cooling down the gases to about  $400^{\circ}$ , at which temperature they pass through the second contact-zone, where the remainder of the  $\text{SO}_2$  is oxidised. This is embodied in the B. P. 1385 of 1901.

Technically we can achieve that object, first, by placing before the present contact-chamber another smaller one, into which the reacting gases enter at a higher temperature, say  $530^{\circ}$ , and where 75 to 80 per cent. of the  $\text{SO}_2$  is changed into  $\text{SO}_3$ . The gases are then cooled down to  $400^{\circ}$ , either from the outside by means of a tubular system or by mixing them with cold gases, which do not disturb the process, and are then passed through the second contact-space, where the remaining 20 to 25 per cent.  $\text{SO}_2$  is almost entirely oxidised. A second, technically practicable way is this: to employ a very long contact-space, in which the gases enter at  $530^{\circ}$  and gradually cool down to about  $430^{\circ}$  before issuing.

As a matter of course the hotter contact-space will not be charged with platinum, but with cheaper contact-substances active at such high temperatures. For that purpose a great many substances were examined for their catalytic properties. The following were found to be active catalysers:—

1. Platinum.
2. Vanadic, molybdic, and tungstic acid, also the complex compounds formed by these acids with each other.
3. The oxides and sulphates of iron, cobalt, nickel, copper, silver, manganese, chromium, uranium, etc.

4. The oxides of cerium, didymium, lathanium, zirconium, thorium, titanium, silicon, and many rare elements.

5. Mixtures of the catalysers with each other.

Among the metals of the platinum group only platinum itself comes into question. Iridium (against the ordinary notion) acts very slowly; so does palladium. Platinum under certain conditions is a good catalyser already at 200°, and is not approached in its action by any other known chemical substance.

Of the substances enumerated under No. 2, vanadic and tungstic acid act about equally well, molybdic acid less so. Of the group No. 3, the sulphates of nickel and cobalt are far the best and are superior even to vanadic acid. Iron acts only in the shape of peroxide. Ferrous compounds are first changed into ferric sulphate by absorbing  $\text{SO}_2$  and O, and this quickly gives up  $\text{SO}_3$ , so that  $\text{Fe}_2\text{O}_3$  remains behind as a catalyser. Copper acts rather less than Ni and Co. Silver sulphate is a good catalyser, uranium much less than the others, and gold not all.

The substances of class 4 are on the whole very slow catalysers, but some, especially freshly precipitated silica, seem to increase the activity of certain catalysers.

Much attention was also given to the so-called *contact-poisons*. Very important observations were made in the laboratory and confirmed in practice. Of the substances examined, Hg and CO were found altogether innocuous. S and  $\text{H}_2\text{O}$ , the latter as steam or sulphuric-acid mist, impeded or stopped the reaction, according to the quantity of S or  $\text{H}_2\text{O}$ ; but when these substances were removed from the gases the contact worked as well as before. As, Se, Te, and Sb are strong contact-poisons, small quantities of which permanently disturb the activity of platinum; they seem to be oxidised to non-volatile oxides which combine with Pt. Besides these elements, another substance occurs in some kinds of pyrites, which acts as a strong platinum poison, but which has not been identified up to the present. Especially selenium and tellurium cause a permanent poisoning. Antimony, thallium, and lead occur only in case of very imperfect purification. Arsenic is a momentary poison, but apparently disappears in course of time, especially when the gases contain traces of moisture.

This is proved by the following fact:—If steam is mixed with the purified pyrites-kiln gases before entering the contact-space, the whole of the arsenic present in the latter is volatilised and the activity of the platinum is restored. Arsenic seems to act as a poison for nearly all other catalysers as well.<sup>1</sup> This is the subject of a Ger. P. application, dated 5th February 1902.

Further efforts were directed towards eliminating the platinum altogether. From the law of the action of masses it follows that, in order to convert at a certain temperature a maximum of  $\text{SO}_2$  into  $\text{SO}_3$ , either the quantity of air should be greatly increased (which would be irrational on account of the expense of propelling the greatly increased mass of gases), *or the  $\text{SO}_3$  formed should be removed from the gases and the latter catalysed again.* This can be effected by cooling the gases after they have left the contact-space and have been partially converted into  $\text{SO}_3$ , removing the  $\text{SO}_3$  by absorption, and passing the gases through a second contact-space. Suppose the temperature of the first contact-space to be  $520^\circ$ , and the contact-substance to be nickel sulphate. Here 80 per cent. of  $\text{SO}_2$  is changed into  $\text{SO}_3$ . After removing the latter, 20 per cent. of the original  $\text{SO}_2$  remains in the gases, which are now passed again over nickel sulphate at  $520^\circ$ ; in this second case again about four-fifths of the 20 per cent. are changed in  $\text{SO}_3$ , or altogether 96 per cent., in lieu of the 80 per cent. possible at  $520^\circ$  with one contact-action. In the second contact it is not necessary to keep the temperature low enough for the most favourable equilibrium of  $\text{SO}_3$ , but here the very large increase of the velocity of reaction at higher temperatures may be utilised.

These facts are laid down in B. P. 2368 of 1901, and the work is then done in one of the following ways (1-4):—

1. (Fig. 506.) The pyrites-kiln gases issuing from the dust-chamber are cooled and purified in  $R_1, R_2, R_3$ , etc., and then passed through a series of pipes E, placed in the dust-chamber or otherwise, where they are heated by the hot burner-gas. These pipes are constructed to act as an economiser, with scrapers for removing any adhering flue-dust. The moving parts of the scrapers are placed in a closed box, or are protected by cup-joints or the like against the  $\text{SO}_2$  gas present in the

<sup>1</sup> Cf. p. 1316, as to the contrary.—G. L.

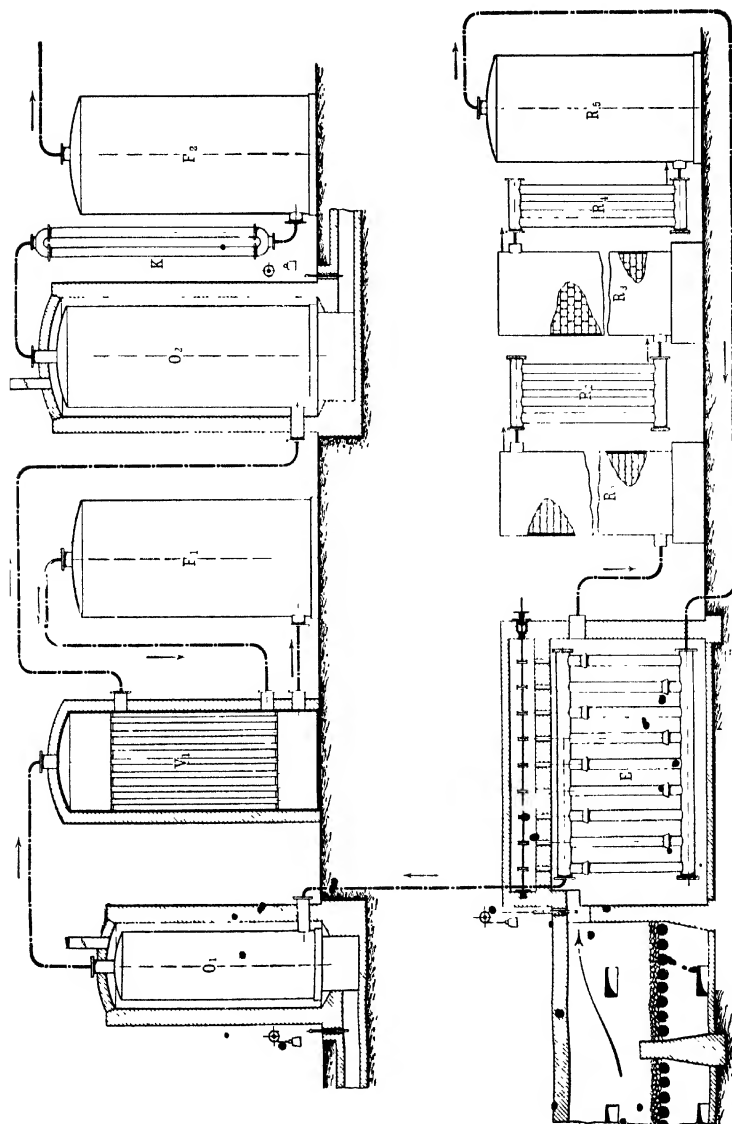


FIG. 506.



dust-chamber. The escape of these gases round the scrapers can also be prevented by slightly compressing the current before entering the chamber and thus producing a very slight minus-pressure therein.

The gases, preferably heated to  $500^{\circ}$  C. in E, now enter the contact-space  $O_1$ . Sometimes it is better to pass them first through an auxiliary heating-apparatus, to provide against any accidents, such as a cooling down of the kilns. In the oxidiser  $O_1$  most of the  $SO_2$  is converted into  $SO_3$ . The gases now pass into the heat-exchanger  $V_1$ , where they are cooled by yielding up their heat to the gases issuing in the opposite direction. The cooled gases are deprived of their  $SO_3$  in  $F_1$ , are then passed back into the heat-exchanger  $V_1$ , if necessary also through a special heat-regulator, and then into contact-space  $O_2$ , where most of the remaining  $SO_2$  is transformed into  $SO_3$ . When issuing from  $O_2$ , the gases are cooled in K and the  $SO_3$  is retained in  $F_2$ , either by strong sulphuric acid or by water or steam.

Of course these processes might be repeated over again, but this would not pay, as the second catalyser already completes the conversion up to 95 per cent., which may be called technically quantitative.

2. The pyrites-kiln gases are cooled and purified in  $R_1$ ,  $R_2$ ,  $R_3$ , then heated up in the heat-exchanger  $V_1$  and passed into the contact-space  $O_2$ , provided with heat-regulator, then passed back into  $V_1$ , where they yield up their heat. After taking out the  $SO_3$  in  $F_2$  the gases are heated in E, passed into  $O_1$ , and absorbed in  $F_1$ .

3. The purified gases are heated in the heat-exchanger  $V_1$ , passed through contact-space  $O_2$ , cooled in K, freed from  $SO_3$  in  $F_2$ , heated again in E, catalysed in  $O_1$ , again passed through  $V_1$ , and at last freed from  $SO_3$  in  $F_1$ .

4. The gases purified in  $R_1$  are heated in E, catalysed in  $O_1$ , cooled in K, freed in  $F_1$  from  $SO_3$  heated in  $V_1$ , catalysed in  $O_2$ , passed back into  $V_1$ , and again freed from  $SO_3$  in  $F_2$ .

Otherwise the gases in modifications 2, 3, and 4 are treated as in 1. The temperature may also be regulated within the contact-spaces from the outside or inside (Ger. P. 113932).

The main point in this new process is that more  $SO_3$  is made with much less catalysing substance without the necessity of

strictly regulating the heat in the contact-space, and that the apparatus for cooling and purifying the gases is very much reduced, as most of the heat is taken out of them anyhow.

A modification of the process, patented in England, France, Belgium, and in the Ger. P. 139554 of the Farbwerke Höchst, and the Amer. P. of Krauss and Von Berneck 700512, consisted in passing pyrites-gases over pyrites-cinders impregnated with ferrous sulphate, at a temperature of about  $350^{\circ}$  C., the cinders being continuously moved forward and falling out desulphurised at one end, and on the other side gases containing  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  escapes. This process (described and illustrated in our last edition, pp. 1052 to 1056) has been dropped by the Höchst factory.

A patent of the Farbwerke Meister, Lucius, and Brüning (Ger. P. 135887 of 7th February 1902) shows how the platinum contact-mass, when *poisoned by arsenic*, can be made to recover its full activity without being removed from the apparatus. If steam is mixed with the hot burner-gases entering the apparatus, the contact-action is in the first instance lowered still further [through the poisonous action of water, cf. p. 1305]; but gradually the whole of the arsenic contained in the platinum as a fixed compound is converted into volatile compounds and escapes with the mixture of  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , issuing from the apparatus. The admixture of steam with the burner-gases is continued until no more arsenic can be traced in the condensing products; then the burner-gases are again introduced in the dry state and the platinum soon recovers its original activity.

Another patent of the same firm (Ger. P. 109728) proceeds as follows. In order to employ less platinum and yet to obtain high yields, the catalytic process is carried out first at higher, then at lower temperatures. In the first zone of reaction the temperature is kept at  $450^{\circ}$  to  $550^{\circ}$ , and here, owing to the great velocity of the reaction, a great portion, say 75 per cent., of the  $\text{SO}_2$  is oxidised to  $\text{SO}_3$  more quickly than the same quantity of platinum could effect at the temperature of  $400^{\circ}$ , which by itself produces a better yield. The gases are now cooled down to  $400^{\circ}$ , and passed into the second zone where the remaining  $\text{SO}_2$  is oxidised. If, for instance, the second, cooler, zone contains half of the quantity of platinum hitherto employed

where there is only one zone of reaction, the same total yield is obtained by employing in the first, hot, zone at most two-tenths of the platinum contained in the second zone, and thus realises a saving of 40 per cent. platinum.

As to the manner in which the *absorption* of  $\text{SO}_3$  is carried out at Höchst, I am enabled to make the following statements. The absorbers are cast-iron vessels with outside cooling-jackets. The  $\text{SO}_3$  gases are passed through the absorbing-liquid in a state of extremely fine division, either by suction or by pressure. If hydrated sulphuric acid is made, only one absorber is employed; for fuming acid two or better three absorbers placed at different heights. The absorbers are fed with acid of more than 93 per cent.  $\text{H}_2\text{SO}_4$ , if fuming acid is to be made; for hydrated acids they are fed with dilute acid or even pure water, run in by a lead pipe. Up to 95 per cent. the acid is as clear as crystal, above that strength it appears turbid through a slight quantity of iron salts taken up from the apparatus, which are insoluble in such highly concentrated acids, and which cannot be removed either by settling or by filtration, but which vanishes on the addition of a slight quantity of water. Some factories mention this expressly in their sale notes for such extra strong acid.

To an inquiry made by me in the middle of 1911, the Höchst Farbwerke replied that they have in the meantime improved the processes above described in several particulars, but no alterations of the principles have taken place. They formerly worked their contact-process with lump burners, but later on by means of mechanical pyrites-burners. This, of course, increased the difficulty of purifying the roasting-gases from flue-dust, arsenic, etc. By introducing appropriate constructions of furnaces, dust-chambers of modern type and gas-filters, these difficulties have been overcome, and extremely pure roasting-gases are now obtained, which greatly increases the duration of the contact-mass and allows of avoiding its reactivation. The catalysis of the roasting-gases is nearly quantitative, as well as the absorption of the  $\text{SO}_3$ -gases, so that the acid contents of the gases escaping into the factory rooms can be easily kept within the limits required by the authorities. The apparatus for absorbing the  $\text{SO}_3$  admits of directly manufacturing sulphuric acid free from arsenic and O.V. of every

degree of concentration. The contact-apparatus proper is very little changed against the description given in the principal patents as quoted *suprà*.

#### IV. The Schröder-Grillo Process.

This process was invented by Dr Schröder and patented by him together with the Aktiengesellschaft für Zinkindustrie, vormals W. Grillo, 1901.

Concerning this system, I have received the following communications from the inventor, Dr Schröder:—

The difficulty of selling liquid sulphur dioxide (*cf.* p. 540) was the reason why the firm Grillo, of Hamborn, already before starting the  $\text{SO}_2$  plant, had taken into consideration the conversion of part of the  $\text{SO}_2$  into sulphuric acid. The application of the lead-chamber process did not seem to be the right thing in this case, because the dilute acid to be manufactured in this way had too low a market value.

On the other hand, the fuming sulphuric acid obtained by contact-processes was at that time still rather expensive, because the preparation of gases containing much  $\text{SO}_2$ , according to Winkler's process of decomposing sulphuric acid, offered technical difficulties, whilst the direct application of roasting-gases, so far as was publicly known, had not yielded satisfactory results.

Under these circumstances the pure sulphur dioxide made at Hamborn from roasting-gases appeared to be an advantageous starting material for the preparation of rich and pure gaseous mixtures for the contact-process. At the request of the firm Grillo, the Badische Anilin- und Sodafabrik at their Ludwigshafen contact-plant made some experiments with gaseous mixtures prepared from Hamborn liquid  $\text{SO}_2$  with admixture of air, but the result was not satisfactory.

But as in the meantime laboratory experiments made at the Hamborn Zinc-works by Hänisch and Schröder had yielded very good results with a comparatively high working capacity of platinum, the firm Grillo resolved to erect an experimental factory for the further development of the contact-process. The starting idea was the assumption that the formerly unsatisfactory results of the contact-process had been principally caused by the fact that the contact between

the gases and the solid reacting medium was not sufficiently intimate for converting approximately all  $\text{SO}_2$  molecules into  $\text{SO}_3$ . The aim was therefore to prevent the gaseous molecules from slipping past the active platinum substance, by means of filling the reaction-space as completely and evenly as possible; and as the ideal state of arranging the platinum molecules suspended at equal distances throughout the reaction-space was naturally impossible to realise, there was no other way of dividing the platinum than that formerly universally applied, viz., spreading the platinum upon porous substances hardly at all active by themselves, and employing these for filling the reaction-space. In practice, deviating from the formerly preferred loose packing of the platinised substances, principally platinised asbestos, this packing was made very firm.

The wrought-iron<sup>1</sup> contact-pipes, 6 in. wide and 13 ft.  $1\frac{1}{2}$  in. long, were filled as follows:—On a bottom of fine stone material a dense plug of platinum asbestos (8 to 10 per cent. Pt) was placed, and firmly compressed by means of a disk fixed to a long rod. In order to exclude the formation of continuous channels, another layer of stone was put in, and again a firm asbestos plug of about 3 in. height. About fifteen double layers of this kind were placed in each pipe, the first portion of the pipe remaining free for a preliminary heating of the gases. A group of five pipes was placed in a furnace in such a manner that the first empty portion lay in the fireplace itself and the second portion, packed as above, was surrounded by the gases issuing from the fireplace. The temperature of the furnace decreased from front to back, and was regulated by means of a pyrometer in such a manner that in the centre a temperature of  $400^\circ$  to  $420^\circ \text{C.}$ , which had been found most favourable for the reaction, was obtained. As the resistance of the contact-mass was bound to be very great, the proportion of the gases was not effected by the hitherto usual fan-blast, but by a cylindrical air-compressor, arranged so that it produced at the same time a mixture of  $\text{SO}_2$  with atmospheric air in the suitable proportion of 25 vol.  $\text{SO}_2$  to 75 vol. air (B. P. 9188 of 1887).

<sup>1</sup> According to information received from users of that process, wrought-iron is strongly acted upon by the gases, in spite of protective coatings. Cast-iron is practically exempt from corrosion by the gases, but such apparatus are liable to sudden, almost explosion-like cracks.—G. L.

The working of the plant showed that the resistance of the contact-mass, with a normal gaseous current, was equal to 0.8 to 1 atm., a somewhat considerable amount, but that, on the other hand, in consequence of the intimate contact of the gases with the platinum, the degree of conversion greatly exceeded all former results. Each contact-pipe produced about 300 to 400 kg.  $\text{SO}_3$  per diem, the yield being about 95 per cent. of the theoretical.

The Ger. P. 42215 had also provided for applying a greater pressure than necessary for overcoming the resistance of the contact-substance in order to prolong the stay of the gases in the contact-space and to favour the union of the active molecules of gases; but this was found superfluous in the experimental plant and was never applied in the plants subsequently erected.

On the strength of the favourable results obtained with the Hamborn experimental plant, the Badische Anilin- und Soda-fabrik in 1887 resolved to carry out the process on the large scale, the firm Grillo renouncing the manufacture of  $\text{SO}_3$  for a period of ten years. Apart from the plant erected at Ludwigshafen in 1887, which has worked for some years, several smaller plants on the same system have been erected by other firms, many of which are even now at work without any change in the contact-action.<sup>1</sup>

When in 1897 the field was again clear for the firm Grillo, it was resolved to start the contact-process again at the Hamborn zinc-works. The old experimental furnace was re-erected, and it was found that the conversion, when employing roasting-gases with 5 to 7 per cent.  $\text{SO}_2$ , was at least as good as with the rich gases formerly used. Thereupon the firm (now "Aktiengesellschaft für Zinkindustrie, vormals Grillo"), together with Dr H. Schröder, started arranging the process for the direct working of blende-roasting gases. As with these dilute gases the process could only pay when greatly reducing the resistance of the contact-mass to the

<sup>1</sup> According to direct information from the Badische, their experiments with the Grillo process were made with inefficient plant and could not be held to be conclusive in any way. Before treating with the firm of Grillo, since 1881, they had already commenced experiments with ordinary burner-gases, and their contract with Grillo did not in any way prevent that firm from working in the last-named direction at any time, even before 1897.—G. L.

propulsion of the gases, without reducing the yield, efforts had to be made to find a sufficiently porous and resisting contact-mass. It had also to be taken into consideration that the danger of a diminution of the contact-action in the case of roasting-gases, even when these are well purified, is much greater than with absolutely pure mixtures of pure  $\text{SO}_2$  and filtered air. It was already known by experience that platinum asbestos, with perfectly pure gases, has an infinitely long action, but that its catalytic action gradually decreases when imperfectly purified gases are employed, and that there was then no means of regenerating its action except by the very troublesome process of transferring the platinum upon fresh asbestos.

This difficulty of regeneration led to abandoning the hitherto employed substrata for platinum in favour of soluble salts, where, owing to the easy renewal of the surface and the porosity of these substances, the regeneration was bound to be much easier than in the case of platinised asbestos, pumice, and the like.

It was soon found that in this way not merely contact-substances of great porosity and easy to regenerate could be obtained, but some of these salts, *e.g.* magnesium sulphate, yielded contact-substances of decidedly better catalytic action than asbestos, pumice, and the like. These contact-substances protected by patents in all countries (B. P. 25158 of 1898), can be made in a very simple manner by mixing or soaking the salts with a dilute platinum solution. The platinum is reduced, without the assistance of other substances, by passing the hot gases containing  $\text{SO}_2$  over the mass; but of course the reduction may be hastened by the admixture of organic substances, such as sugar, oil, glue, etc., afterwards burned, and the porosity of the mass is thereby at the same time increased.

To decrease the resistance against the passage of the gases, much larger pipes are now employed. But as the activity of the platinum was found not to be fully utilised, greater dilutions of platinum in the magnesium sulphate masses were employed; less than one-hundredth of the percentage of platinum formerly employed is sufficient without any detriment to the contact-action. Afterwards, in lieu of a number of pipes, a single

contact-chamber was introduced, as already described in Deacon's patent 753 and 1682 of 1871 (cf. *suprà*, pp. 1283 *et seq.*). The apparatus was constructed in such a manner that the  $\text{SO}_2$  gases were first heated up to the requisite temperature in a tubular apparatus and then passed into the contact-space. As the reaction proceeds vividly, a quantity of heat being set free by itself, the contact-apparatus need not be heated but merely protected against radiation. But the yield in these apparatus was found to be only 85 to 90 per cent. of the theoretical. Although on principle a preliminary heating of the gases to  $250^\circ \text{C.}$  ought to suffice, since the formation of  $\text{SO}_3$  commences to set in just over  $200^\circ$ , and more and more heat is generated by the reaction itself, it was established by gas-analyses and temperature determinations that the reaction progresses only in the centre of the cylinders, whilst the gases rising near the walls, in spite of good insulation, lose more heat than can be spared for the reaction.<sup>1</sup>

This drawback could be avoided by a compulsory mixture of the gases in simple or composite cylinder apparatus, as described in the B. P. 17034 of 1900. These apparatus have been found to answer very well, and to act in no way inferior to the composite pipe apparatus. The resistance of the contact-mass to the propulsion of the gases can be reduced by a suitable increase of section in such a way that revolving apparatus (fan-blowers) are quite sufficient for that purpose.

A further improvement in the contact-mass was attained by building up the mass in the molten state in the contact-apparatus itself by means of a hot current of gas or air (B. P. 10412 of 1901). Thus not merely a high degree of porosity is attained, but the caking of the mass prevents the strong gaseous current from carrying away single portions of it.

The absorption of the vapour of  $\text{SO}_3$  formed takes place after cooling in iron apparatus by means of sulphuric acid, either by surface-action or submersion or running the absorbing acid down a tower or spraying it in the stream of  $\text{SO}_3$  vapour. If no dilute sulphuric acid for this purpose is yielded by

<sup>1</sup> The apparatus erected at Ludwigshafen for the Grillo-Schröder system by Dr Schröder himself did not work as above, but was expressly arranged to keep the temperature of the outer contact-oven as uniform as possible at all points.—G. L.



another part of the works, it is prepared by mixing part of the strong acid previously obtained with water and cooling.

For cooling, purifying, and drying the roasting-gases before introducing them into the contact-process in many cases the process prescribed by Rath (Ger. P. 22118) has been found sufficient, consisting in slowly filtering the gases through coke moistened with sulphuric acid. The low velocity of the gases, at most 2.3 in. per second, requires a very wide section of the low towers and admits of employing a very fine coke-packing, without any considerable resistance to the passage of the gases. In order to increase the filtering action, it is possible to employ apparatus containing a fibrous material like asbestos or cotton-wool. Such a purification in connection with drying the gases by sulphuric acid is quite sufficient for the removal of flue-dust, mist, sublimates, and moisture from the gases, but not for purifying the gases from injurious gaseous constituents evolved in the roasting of some ores. The most injurious of such gases has been found at Hamborn to be silicon tetrafluoride evolved in the roasting of ores containing fluorine. Unless previously removed, that gas is decomposed within the contact-mass in such a manner that dense layers of silica are formed which envelop the contact-substance and render it inactive.

Apart from silicon tetrafluoride, arseniuretted hydrogen must be taken into consideration, whose injurious action upon the catalytical property of platinum has been long known. At Hamborn and in many other places that gas has not been noticed, probably because the conditions of its formation (application of iron gas-pipes, etc.) were not present. The sublimed  $As_2O_3$  contained in the gases is easily removed by filtration together with the other constituents of flue-dust.

If in consequence of insufficient purification of the gases the contact-action is gradually weakened, the contact-mass must be from time to time freshened up, especially in order to counteract the incrustation with silica. This is most conveniently done by washing the mass with a dilute solution of aqua regia, whereby the platinum is freed from the surrounding silica, and at the same time the porosity of the surface is renewed. Any slight traces of arsenic absorbed by the contact-mass are equally removed by the aqua regia, being converted into

$\text{AsCl}_3$ , which volatilises in the hot current of air when heating up the contact-mass.

If ultimately the percentage of silica, iron, etc., becomes so large that the regeneration in the just-mentioned manner is not sufficient, the platinum and the salt must be separated from the impurities in the wet way.

In the beginning of 1902, ten factories were working the Grillo-Schröder process (four of them in Germany), and another twelve factories (again four in Germany) were in course of erection.

Thus far I have translated verbatim Dr Schröder's communication; I shall now subjoin abstracts of the various patents taken out for this process.

Grillo and Schröder (B. P. 25158 of 1898) produce a contact-mass by an intimate mixture of a soluble salt not changed by the agents in question, such as sulphates or phosphates, with finely divided platinum in the following manner:—The salt (*e.g.* sodium sulphate)<sup>1</sup> is dissolved in water, mixed with platinic chloride in the proper proportion, and the whole evaporated to dryness, breaking up the crusts so formed into pieces of uniform granular size. The separation of the platinum in a metallic state, of very high grade of division, takes place on heating the contact-mass when the process is started. These contact-masses act perfectly well even when containing only 0.1 per cent. of platinum, and when rendered inactive they are simply dissolved in water, whereupon the platinum separates out in a metallic state and can be employed over and over again.

Their Ger. P. 115333 describes the removal of arsenic, antimony, mercury, etc., from the contact-mass in the contact-space itself by means of a current of chlorine at the ordinary temperature of that space, or somewhat below. Previously, any oxides of those metals present may be reduced to the metallic state by means of coal-gas, carbon monoxide, etc.

A further patent, B. P. 17034 of 1900, by the Aktien-gesellschaft Grillo and M. Schröder gives the following descriptions:—Gases from pyrites-kilns or similar gases, with about 6 per cent.  $\text{SO}_2$ , pass into the bottom of a chamber, where they

<sup>1</sup> Recently magnesium sulphate seems to be considered the most suitable salt for this purpose.

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are heated to  $260^{\circ}$  or  $280^{\circ}$  C., thereupon through several layers of contact-substance spread on perforated iron plates, and from this, now in the state of  $\text{SO}_3$ , to the absorbers. The perforated metallic diaphragms produce a good mixture of the gases and a uniform temperature which is controlled by laterally introduced pyrometers. The temperature during the reaction may rise to  $500^{\circ}$  or  $520^{\circ}$ , the gases leave at  $350^{\circ}$  or  $400^{\circ}$  C. A larger style of apparatus consists of several vessels connected by pipes, alternately above and below the layer of the contact-substance. The mixture of the gases passing from any one chamber to the next in series is promoted by causing them to flow through a narrow passage into a larger space before traversing the contact-matter next in turn. In this manner a conversion of 96 to 98 per cent. is said to be effected, against only 85 to 90 per cent. where such distribution is not employed, in consequence of excessive heating in the centre and cooling below the proper temperature at the walls.

The claims under this patent are as follows :--

1. In the catalytic process of making sulphuric acid or its anhydride without regulating the temperature of the reaction from the outside, the use of a contact-apparatus consisting of a vessel or chamber provided with solid partitions having one or more openings through which the preheated or flowing contact-gases are constrained to pass after they have passed through a quantity of contact-mass for the purpose of being thoroughly mixed previous to passing into another quantity of the contact-mass.

2. For the purpose referred to in claim 1, a contact-apparatus consisting of a number of vessels charged with contact-mass and connected by pipes in such a manner that the gases in passing from one vessel to the adjoining one are thoroughly mixed.

A still more porous mass than usual is obtained by Grillo and Schröder (B. P. 10412 of 1901) by forming the pores in the "carrier" whilst this is still in the pasty condition and in the process of drying, by forcing a gaseous current through the mass at a rate similar to that employed in the converter during normal working. Suitable substances as "carriers," apart from the salts mentioned in the patents, are clay, gypsum made into a paste with water, also salts melting in their own

water of crystallisation. The preparation of the contact-mass may be carried out in the contact-oven itself. (A Ger. P. by Neuendorff, 127846, runs on similar lines, employing salts of Ca, Ba, Sr, other than the sulphates, with  $\text{SO}_2$ , air, and steam or sulphuric-acid vapour at a high temperature.)

Ger. P. 138695 of the Grillo-Schröder Company describes an improvement in their contact-apparatus, consisting in arranging perforated partition walls in the spaces between each two layers of contact-mass, by which means the gases are more intimately mixed through during their passage over that mass.

Several important contributions concerning the Schröder process were made to the New York Section of the Society of Chemical Industry, and are published in its *Journal*, 1903, pp. 348 *et seq.*, by Fr. Meyer, G. C. Stone, and C. L. Reese. The first of these is of a historical kind, and adds nothing of importance to what has been said before on that process. I here give an abstract of the other two papers.

Stone points out that in the Schröder process the following impurities are most injurious: arsenic (which does not occur in the blende used at the original works at Hamborn),  $\text{SiF}_4$ ,  $\text{HCl}$ , and  $\text{Cl}$ . Arsenic permanently ruins the contact-mass, the other impurities have only a temporary effect which vanishes when pure gases are used. (His Amer. Ps. 711187 and 711188 prescribe removing the arsenic vapours by cooling the burner-gases down to a temperature at which the arsenic is condensed, and retaining it in a filtering-medium which is afterwards freed from arsenic by heating.) With properly purified gas the mass gives a yield of 96 per cent. and more even after a year's run. When it is necessary to regenerate it, it is spread on a cement floor, made into a stiff paste with a mixture of dilute nitric acid, hydrochloric acid, and sugar, allowed to stand for a few days, heated to expel water and acids, cooled and crushed. It is then often slightly better than when first used. According to that author there were in 1903, 23 Schröder plants built or building (7 in Germany, 2 in Russia, 1 in Poland, 1 in Italy, 2 in France, 1 in Chili, 1 in Mexico, 2 in South Africa, 6 in the United States). Since then other plants have been erected, e.g. in Switzerland. Some are using blende, some pyrites, some brimstone, and one a low-grade gold-ore. Their degree of purity being very different, different methods of purification

are used. In every case there is a dust-catcher next to the burners, then a cooler by which the temperature is reduced to that of the air, then scrubbers or washing-towers for washing and drying the gas, then filters for removing most of the arsenic, selenium, etc. The gas is drawn from the filters and forced through the preheaters, in which it is got up to  $300^{\circ}$  to  $400^{\circ}$  C., when it immediately enters the converter. There is no necessity for regulating the temperature in the sectional converters, which are sometimes large enough to produce 10 tons acid of  $66^{\circ}$  Bé. in one day. From the converter the gas passes to a cooler, where it is cooled down to about  $50^{\circ}$  C., and then to the absorbers. When only acid of less than 100 per cent.  $\text{H}_2\text{SO}_4$  is to be made, some form of scrubbing-tower is the best absorber; for fuming acid horizontal cylinders, followed by a tower, are most suitable, and acid up to 40 per cent. free  $\text{SO}_3$  can be made here directly. Every hour the  $\text{SO}_2$  in the entering and exit gases is estimated by the Reich test. The purity of the gases is best ascertained by blowing a small current of the gas continuously through a tube filled with absorbent cotton, which ought not to show a deposit or discoloration after several weeks.

The conversion is good and uniform, e.g. at one plant for a month's run minimum 94.47, maximum 97.76, average 96.68; at another in seventy-seven days' run minimum 91.48, maximum 97.43, average 95.39 per cent. It remains the same whether the gas contains only 3 to 4 per cent. or 6 to 7 per cent.  $\text{SO}_2$ . The stops from all causes do not exceed twenty hours per month. The acid made was 95.01 per cent. of the sulphur burned. The cost of the plant is less than that of a lead chamber and concentrating-plant. For acid above  $60^{\circ}$  Bé. the process is cheaper than the lead-chamber process; from  $60^{\circ}$  Bé. below there is no advantage. A plant is now being built for combining the Schröder process with chambers, so as to produce strong acid without concentrating-plant.

Reese describes his experimental investigations on the Schröder process. His results are most interesting, but partly differ so much from those of other observers that further observations seem called for. Thus he states that the gases need not be dried, but may even be saturated with moisture without affecting the conversion in any way, although this

cannot be carried out in practice, owing to the necessity of using iron pipes.  $\text{CCl}_4$  and  $\text{CO}$  have no effect, nor has sulphur in a finely divided form.  $\text{HCl}$  reduces the conversion at once to 42 per cent.,  $\text{Cl}$  to 57 per cent.;  $\text{SiF}_4$  acts similarly: but in all these cases, if pure gas is introduced, the conversion gradually rises again to the normal point. Arsenic is extremely injurious; it may reduce the contact-action to zero, but it can be removed from the contact-mass by a stream of  $\text{HCl}$ , best mixed with  $\text{SO}_2$  (burner-gas). It is found in the shape of a *mist*, together with  $\text{PbSO}_4$ ,  $\text{SiF}_4$ ,  $\text{HCl}$ ,  $\text{S}$ , and  $\text{Se}$ . This mist cannot be removed by scrubbing with either water or sulphuric acid, but by wet filters [evidently made of asbestos or cotton-wool, *cf.* below]. By these the gas is purified to such an extent from solid and liquid substances that a beam of sunlight from a lens cannot be seen when passed through a vessel containing the gas [Tyndall's test]. In this case the contact-mass lasts indefinitely. Another test is to allow the gas to pass continuously through a tube containing absorbent cotton, when any acid or other impurity can be seen after a short time deposited on the cotton [*cf. supra*].

The reaction starts at  $330^\circ$  to  $340^\circ \text{C.}$ , and is at its best at  $425^\circ$ , but there is very little difference between  $400^\circ$  and  $435^\circ \text{C.}$  With impaired contact-mass a higher temperature is required to start the reaction. No cooling is necessary with the Schröder contact-mass when used in sectional converters, otherwise than that resulting from radiation. It is simply necessary to preheat the gas to about  $400^\circ \text{C.}$ , and the converters do the rest. Eighty-five to 90 per cent. of the conversion takes place in the first of the four sections, where the temperature rises about  $100^\circ \text{C.}$ ; it gradually falls in the other sections, and the gases leave the converter below the temperature at which they enter.

The absorption of  $\text{SO}_3$  by water is not so good as might be expected. The rate of absorption increases with the strength of the sulphuric acid formed, and is at a maximum when the vapour-tension is zero. Evidently  $\text{SO}_3$  unites with the vapour of water, forming minute globules of  $\text{H}_2\text{SO}_4$ , which cannot be satisfactorily absorbed by acid of any strength or even alkali, but perfectly by means of several layers of wet asbestos or cotton-wool.

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The Schröder-Grillo process is applied in Chile (Guayacan) for transforming the  $\text{SO}_2$  in the gases from roasting copper regulus into sulphuric acid. For each kilogram of contact-mass in twenty-seven hours 2250 kg. commercial acid of 93 to 96 per cent. is obtained, with an expenditure of  $\frac{3}{4}$  kg. fuel.

The factory at Uetikon in Switzerland, which is surrounded by vineyards and is thereby compelled to use the utmost precaution in the matter of escapes of acid gases, sends the exit gases from their Schröder-Grillo plant, in which they convert 96 per cent. of the  $\text{SO}_2$  into fuming O.V. (20 per cent.  $\text{SO}_3$ ), into their lead-chambers, in order to retain even the last few per cents. of  $\text{SO}_2$  which might do damage to the vines.

The following list of the  $\text{SO}_3$  patents obtained by the Grillo Company has been communicated to me by that firm in 1911:—

1. *Contact-substances for Catalytic Processes.*—Germany 102244; France 283496; Belgium 140984; Austria 565; Hungary 15502; Italy 54742; Spain 25637.

2. *Improvements for Recovering Sulphuric Acid, etc.*—England 25158 of 1898; Natal 23 of 1901; Cape Colony 1280.

3. *Contact-furnaces.*—Germany 138695; France 304530; Belgium 152713; Great Britain 17034 of 1900; Natal 157 of 1901; Cape Colony 1445; Italy 57464; Spain 26728; Switzerland 22762.

4. *Apparatus for the catalytic production of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ .* Austria 12287; Russia 8372, 8373, and 8446.

5. *Dry Purification of Contact-substances.*—115333.

6. *Processes for Preparing Contact-substances.*—Germany 128554; France 311689; Belgium 156974, Great Britain 10412 of 1901; Natal 156 of 1901; Cape Colony 1446; Peru 96; Chile? U. S. America?

### V. Process of the Verein Chemischer Fabriken in Mannheim.

These processes are inventions partly of Dr Hasenbach, partly of Dr A. Clemm, both of them connected with the Mannheim Verein.

Their patents are:—

1. Ger. P. 106715 of 1898; B. P. 17266 of 1898; Austr. P. 484; Fr. P. 280393; Belg. P. 137510 for the removal of arsenic

from burner-gasses by passing these through red-hot ferric oxide, preferably in the shape of pyrites-cinders, or through chromic oxide or other oxides, forming fire- and acid-proof compounds with the oxides of arsenic.

2. Ger. P. 107995 of 1898; B. P. 17255 of 1898; Austr. P. 484; Fr. P. 280393; Belg. P. 137510; Amer. P. 681698 *for preparing*  $\text{SO}_3$  from  $\text{SO}_2$  and air by passing the gases over red-hot ferric oxide (pyrites cinders), as they come from the pyrites-burners.

3. Ger. P. 108445 of 1898; B. P. 1859 of 1899; Austr. P. 2519; Fr. P. 285459; Belg. P. 140696; Amer. P. 670559 describes a *pyrites-kiln*, with an air-drying apparatus, with air-tight working-doors and an iron casing, in order to prevent the access of undried air from without.

(The patents 1, 2, and 3, according to the statements I have received, have fulfilled their purpose and are in regular use, in Germany, Austria, England, France, Belgium, Russia, and America.)

4. Ger. P. 108446 (1898); B. P. 3185 (1899); Austr. P. 483; Fr. P. 280393 (addition); Belg. P. 140695. The process described in Ger. P. 108445 may be modified by diluting the burner-gasses with dry, preheated air.

(This patent is not of special value, although the observation on which it is founded is quite correct.)

5. Ger. P. 136134 (1899); B. P. 24748 (1899); Austr. P. 10510; Fr. P. 295238 and addition; Belg. P. 147437; Amer. P. 690133 and 729735 describes the *combination of a ferric-oxide and a platinum contact-apparatus*. The gases pass first through the former, then through a dry pumice or asbestos filter (in order to retain foggy impurities), then through a heating-apparatus, and lastly through a second contact-apparatus, charged with platinised acid- and fire-proof tissue, either from above or from below.

(This process is in successful operation, both in Germany and in other countries.)

6. Ger. P. 142410 (1899); B. P. 4610 (1901); Austr. P. 10511; Fr. P. 295238 (addition); Belg. P. 155501 protect the replacing of ferric oxide as contact-substance, by cupric or chromic oxide, or mixtures of these with each other or the sulphates formed. (Of no special importance.)

7. Ger. P. 142855 (1901); B. P. 16206 (1902); Austr. P.



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15339; Fr. P. 323491; Belg. P. 164891; Amer. P. 752165 describe a contact-apparatus, containing platfinised asbestos-tissue, extended in cast-iron frames; between each two such frames, wide-meshed iron tissue in thin wrought-iron frames is placed, in order to prevent the asbestos tissue from bulging out upwards or downwards. The surfaces of contact between the frames are smoothly planed, so that the gases cannot take a wrong road, and the frames are so adjusted that they can be slid and singly taken out for being changed, without interrupting the work.

(This apparatus is in successful operation both in Germany and abroad.)

8. Ger. P. 154084 (1902); Austr. P. 484; Fr. P. 280393; Belg. P. 137510 provide for the application of ferric oxide containing arsenic, such oxide being a better catalyser than pure ferric oxide (Amer. P. 758844 by Lunge and Pollitt).

(This patent has been dropped.)

9. B. P. 15151 of 1899; Amer. P. 716985.

Employment of cupric sulphate for the manufacture of  $\text{SO}_3$ .

(This process was not patented in Germany but in the United States, where the patent is still valid.)

The following communication concerning that system has been made to me by the Verein Chemischer Fabriken in Mannheim for the 1903 edition of this work:—

“The principles underlying our process are as follows:—(1)

• Roasting the pyrites with dried air, in order to produce dry kiln-gases. (2) Graduated conversion of sulphur dioxide into sulphur trioxide in two separate contact-spaces, one of which is charged with ferric oxide, the other with platinum. The  $\text{SO}_3$  formed in each of these is best absorbed in separate absorbing-plant. (3) Behind the absorbing-apparatus for the  $\text{SO}_3$  formed in the ferric oxide contact-space there is a filter for retaining from the gases any impurities injurious to the platinum contact.

“These principles are embodied in our patents [quoted *supra*, and abstracted below]. The apparatus constructed for carrying them into practice consists of a pyrites-kiln, differing from ordinary pyrites-kilns by being completely cased in iron and by such a construction of all openings that the doors can be tightly pressed against faced frames, in order to prevent as much as

possible the entrance of undried air through the brickwork and the working holes.

"The air necessary for burning the pyrites is introduced by means of pipes underneath the grates. This air is dried in towers fed with concentrated sulphuric acid. The roasting-gases enter still hot into a perpendicular iron-cased chamber, filled with ferric oxide in pieces, to a height of 7 to 10 feet. This oxide [pyrites cinders] rests on a revolving grate, by which the spent contact-mass can be removed, the fresh contact-mass being fed in at the top. Here the conversion of the  $\text{SO}_2$  into  $\text{SO}_3$  is brought about to the extent of 60 or 65 per cent., and at the same time the arsenic is chemically fixed by the ferric oxide.

"From this chamber the gases enter into cooling-apparatus and thereupon into absorbers, where the  $\text{SO}_3$  formed by the ferric-oxide contact is retained. At the end of the absorbing-apparatus a fan-blast is placed which draws the gases through the various apparatus hitherto described, and propels them through the following apparatus. The gases at this stage are very pure, but they contain still traces of impurities, not shown by chemical analysis, which in course of time might injure the activity of the platinum contact-substance, and small quantities of uncondensed sulphuric acid [anhydride] which must be removed before the gases act upon the platinum.

"This purification of the gases is brought about by filtration through porous, granular, or fibrous substances. After having been thus filtered, the gases possess such a degree of purity that the activity of the platinum contact-mass is secured for a very long period. The filtered gases are heated up by the heat of the kiln-gases or by a direct fire to the degree necessary for the reaction and now enter the platinum contact-space, in which the remainder of the  $\text{SO}_2$  is converted into  $\text{SO}_3$ . From here the gases pass through a cooler and into an absorber, where the newly formed  $\text{SO}_3$  is retained, and ultimately into a chimney."

We shall complete this sketch by abstracts of the patent specifications.

B. P. 17266 of 10th August 1898 prescribes burning pyrites in ordinary furnaces, to which air is admitted previously heated and thoroughly dried. The hot roaster-gases are at once conducted over a contact-substance containing ferric oxide

(preferably fresh burnt pyrites-waste) placed in an oxidation chamber to which external heat is not applied. Pyrites-waste affords also an excellent means for extracting, in a technically perfect manner, the arsenic from pyrites-kiln gases, so that a large yield, free from arsenic, is obtained from the initial materials containing arsenic, if, in passing the gases over the burnt ore, the production of comparatively large quantities of sulphuric acid be as much as possible avoided.

B. P. 1859 of 26th January 1899 describes the chambers for containing the burnt pyrites with their revolving grates, their iron casing, and their devices for excluding all air except that which has been desiccated.

B. P. 3185 of 13th February 1899 describes another modification of the contact-furnace, with more admission of air. The ordinary roasting-gases, containing 6 or 8 per cent.  $\text{SO}_2$ , are to be diluted with desiccated air, either when in the reaction-chamber or before entering it, so as to produce a gaseous mixture containing from 2 to 3 per cent. by volume of  $\text{SO}_2$ , whereby the production of  $\text{SO}_3$  is considerably enhanced.

According to A. Clemm's B. P. 15151 of 1899, a mixture of  $\text{SO}_2$  and O or acid is passed over red-hot cupric sulphate, previously moulded into convenient forms with clay or gypsum.

A. Clemm and the Verein Chemischer Fabriken in Mannheim (B. P. 24748 of 1899) conduct the gases from the pyrites-kilns, with admission of dried air, over highly heated burnt pyrites, then subject them to dry filtering over pumice-stone, asbestos, or the like, and afterwards admit them to a second contact-apparatus, charged with platinum contact-substance. The  $\text{SO}_3$  formed in the first contact by the action of ferric oxide may be absorbed before passing the gases on to the platinum contact-chamber. (This seems to be essential, in order to prevent deterioration of the platinum catalyst, the gases being reheated if necessary.) The platinum contact-mass is preferably platinised grating or network of platinised fabric carried by frames. The Verein, in B. P. 18205 of 1902, describes an apparatus charged with platinum asbestos so arranged that the contact with the gases is as perfect as possible, without employing much pressure. (Cf. *suprà*, pp. 1401 *et seq.*, their new apparatus protected by Ger. P. 142855.)

The Mannheimer Verein Chemischer Fabriken (B. P. 4610

of 1901; Ger. P. 142410) also patents the use of cupric oxide, chromic oxide, or manganese oxide, or a mixture of the three, or their sulphates, as contact-substances, and also for filtering the hot roasting-gases.

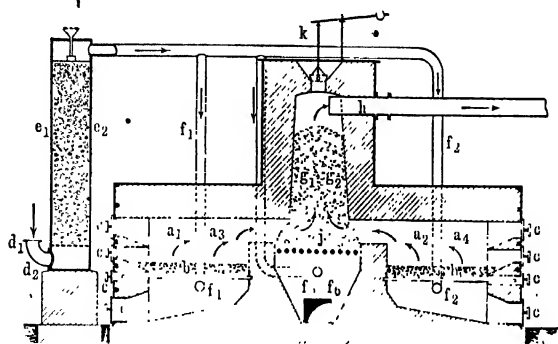


FIG. 507.

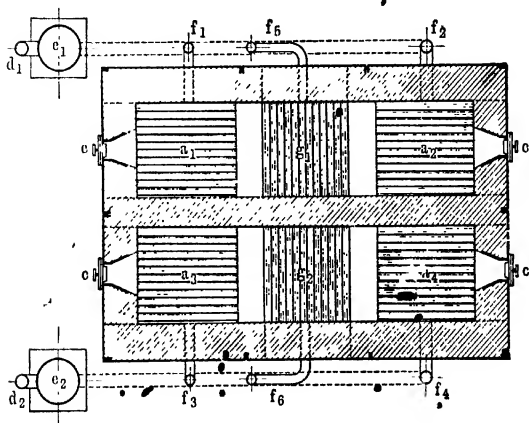


FIG. 508.

We shall now describe more in detail the pyrites-kilns and contact-chambers. In Figs. 507 and 508  $a_1, a_2, a_3, a_4$  are burners,  $b$  the pyrites burning therein. All openings are made tight by asbestos joints and screw-bolts, the doors being pressed against planed surfaces; this is shown at  $c$ . The air enters at

$d_1, d_2$ , in drying-towers  $e_1, e_2$ , and is carried by pipes  $f_1, f_2, f_3, f_4$  underneath the burner-grates. Further pipes  $f_5, f_6$ , communicate with the contact-chamber, in case this is equally to be supplied with dried air, and in a similar manner this can be supplied over the layer of burning pyrites. The gases issuing from the burners traverse upright chambers,  $g_1, g_2$ , filled with pyrites-cinders, where the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  takes place; they are then taken by  $h$  to the condensing-apparatus. The whole furnace is cased with iron, in order to prevent any air from penetrating through the brickwork. Through  $k$  fresh pyrites-cinders are charged into  $g_1, g_2$ , and through the revolving grate  $j$  the spent cinders are removed. Further openings may be provided in the burner or contact-chamber for diluting with air. The air is preferably heated before entering the apparatus.

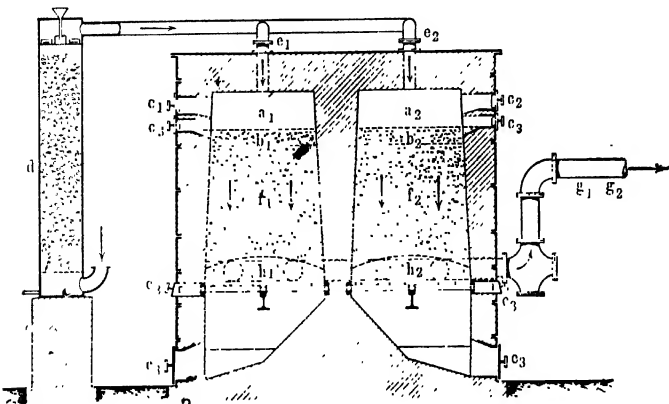


FIG. 509.

Figs. 509 to 511 show how the contact-chamber may be placed underneath the burners, and is traversed by the burner-gases from the top downwards. In  $a_1$  and  $a_2$  the burning takes place;  $b_1$  and  $b_2$ , the burning pyrites;  $c_1$  and  $c_2$ , the air-tight charging-doors;  $c_3$ , the other working-door, equally air-tight. In this case the pyrites burns from the top downwards. The necessary air is dried in tower  $d$  and passed into the apparatus through pipes  $e_1$  and  $e_2$ . The gases generated in layers  $b_1$  and  $b_2$  pass through the layers of burnt ore  $f_1$  and  $f_2$ , where the con-

version of  $\text{SO}_2$  into  $\text{SO}_3$  takes place, and then go through  $g_1$  and  $g_2$  to the condensers. The spent oxide is removed by the revolving grates  $h_1$  and  $h_2$ . This furnace must also be cased in iron.

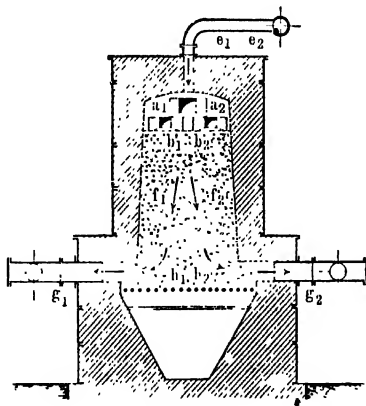


FIG. 510.

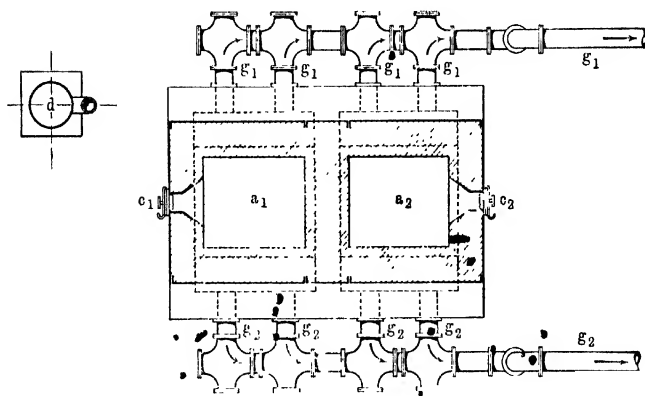


FIG. 511.

Experiments made by Lunge and Pollitt (cf. *suprà*, p. 1316) have confirmed the fact that the degree of conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is strongly reduced by the least amount of moisture present, either in the ferric oxide or in the gases. This degree

remains the same, whether the gases contain up to 13 per cent. or down to 2 per cent.  $\text{SO}_2$  by volume. The best temperature for the reaction is about  $620^\circ \text{C}$ . The presence of cupric oxide or arsenic (which is no doubt converted into ferric arseniate) increases the catalytic action, the arsenic more than the copper. Probably the  $\text{SO}_2$  is first oxidised to  $\text{SO}_3$  at the expense of the arseniate, and the arsenite thereby formed is again oxidised to arseniate by atmospheric oxygen. (This influence of arsenic in promoting the contact-action, found by Lunge and Pollitt, forms the subject of a Ger. P. 154084 taken out by the Mannheimer Verein Chemischer Fabriken, but abandoned later on.)

From a private source I have received the following communications on the working of the Mannheim process in America. Every furnace gets through  $6\frac{1}{2}$  to 7 tons Rio Tinto ore (containing arsenic and copper) *per diem*, the burner-gases testing 7 or 8 per cent.  $\text{SO}_2$ . After passing through the ferric-oxide contact-shaft, which is kept at a temperature of  $600^\circ$ , they show from 3 to 3.6 per cent.  $\text{SO}_2$ . They now pass through an iron cooling-tower and through three wash-towers, where the  $\text{SO}_3$  is taken out by sulphuric acid (96 per cent.  $\text{H}_2\text{SO}_4$ ). Then follows a purification from arsenic by means of blast-furnace scoria, containing sulphides, and a further heating to  $540^\circ$  or  $560^\circ$ , after which the gases pass through thirty pieces of asbestos cloth, coated with platinum black. The exit-gases are cooled by being used for getting up to temperature of the ferric-oxide shaft, and are deprived of the last  $\text{SO}_2$ . The whole of the apparatus is made of cast-iron. The pyrites is employed in the shape of lumps, and is burned down to 3 or 4 per cent. S; the air is drawn through it by a fan-blast. The platinised asbestos cloths are washed with 2 per cent. muriatic acid once in two months, dried and cased over again. Every furnace works with 750 g. platinum black divided upon thirty cloths; it is obtained in the proper state by means of sodium formiate. The yield of acid is 118 to 130 lbs. from 100 ore, calculated as 100 per cent.  $\text{H}_2\text{SO}_4$ . A drawback is that the acid is not clear and contains 0.7 per cent. ferric sulphate, which is too much for the manufacture of explosives; this seems to happen only at the American works, which utilise their acid for the refining of petroleum (the Standard Oil Company has twelve such furnaces), and where that impurity does no harm. The idea can be

obtained with 28 per cent.  $\text{SO}_3$  *in maximo* : if this is exceeded, the apparatus is soon damaged, but higher strengths can be obtained by distilling the oleum.

According to Wilke (*J. Soc. Chem. Ind.*, 1906, p. 4), the first American plant for the Mannheim process was erected by Schoellkopf & Company at Buffalo, and consisted of one unit with a capacity of 1000 tons of sulphuric acid ; it has since then been enlarged to four times its original capacity. Four other firms have adopted this process, and there were then (1906) in use 22 units with a capacity of 35,000 tons, and in the course of construction 10 more units with a capacity of 16,000 tons—all this in a little over two years from the first introduction of that process, which is very much praised by Wilke.

#### VI. *The Freiberg Process.*

Through the kindness of the late Professor Clemens Winkler I am enabled to give the following authentic communications on the introduction and development of the manufacture of sulphuric anhydride by the contact-process in the Muldenerhütte at Freiberg, on the strength of official documents, all of which had hitherto remained unpublished.

The first experiments for carrying out the process of combining  $\text{SO}_2$  and O by means of the process published by Winkler in 1875 (*Dingl. polyt. J.*, ccxviii, p. 128) on a manufacturing scale began on 18th December 1876. As described in that publication, sulphuric acid of 66° B $\acute{e}$ . was decomposed by strong heat, the resulting gaseous mixture was dried and conducted over moderately heated platinum asbestos. The  $\text{SO}_3$  thus obtained was at first condensed as such, later on much more conveniently by absorption in concentrated sulphuric acid.

The results were so satisfactory that, on 9th March 1878, the erection of a larger plant was resolved upon. But almost exactly at the same time, on 10th March 1878, the Royal Mining Office received a report by Cl. Winkler, in which he requested them to take notice of an observation made by him which would enable the process of manufacturing anhydride to be carried on in a new and much more practicable form. This report contains the following passage :—“ *The undersigned has succeeded in achieving a result regarded as impossible according*



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to former experiments, viz., the production of sulphuric anhydride from a mixture of sulphur dioxide and atmospheric air." After discussing at length the points important for the success of the new process, the author gives a description of the way in which the process can be carried out on the large scale. He here discusses, first, the quality of the gaseous mixture obtained in the kilns; secondly, the mode of propelling the gases; thirdly, the purification and drying of the gases; fourthly, the transformation of  $\text{SO}_2$  into  $\text{SO}_3$ ; fifthly, the condensation of the  $\text{SO}_3$ .

The production of sulphuric anhydride from pyrites-kiln gases at the Freiberg works commenced on a small scale in the beginning of December 1878, on a larger scale on 1st February 1879. But as there were many difficulties to overcome and many changes became necessary in the plant, the commencement of a continuous manufacture dates only from 13th December 1879. On 3rd October 1881 a larger plant was started, utilising a proposal found successful in the meantime for removing the last traces of flue-dust (which interferes with the efficiency of the contact-substance) by filtering the gases through carded cotton-wool.

Soon after the Freiberg works had commenced trying the manufacture of  $\text{SO}_3$  from kiln-gases, the Rhenania works at Stolberg entered upon this path, with mutual understanding and partial exchange of experiences. At Stolberg, vertical contact-apparatus was preferred to the horizontal pipes used at Freiberg. The filtration by cotton-wool and the employment of platinised porcelain (see below) has also remained a speciality of the Freiberg works.

The manufacture of sulphuric anhydride is now carried out at the Muldeneshütte, near Freiberg, as follows:—

1. *Roasting-gas.*—Since 1879 the gases from ordinary pyrites-kilns, containing a little arsenic, have been employed for this purpose.

2. *Propelling of the Gas.*—Since 1879 this has been effected by a steam-driven fan-blast placed between the purifiers and the contact-apparatus, so that the gas is aspirated from the kilns through the purifiers, and propelled under pressure into the contact-pipes and the absorbing-towers.

3. *Purification of the Gases.*—This is effected exclusively by filtration, without any washing- or drying-apparatus. This has

been done since 1881, ultimately through the employment of carded cotton-wool, which retains the last traces of flue-dust without the necessity of frequent renewal (probably gun-cotton might be employed for the same purpose). At first it was thought necessary to wash and dry the gases, after previously removing most of the flue-dust, by towers fed with sulphuric acid of  $66^{\circ}$  B $\acute{e}$ .; but this caused the cotton-wool to be gradually moistened and destroyed by the slight quantity of sulphuric acid carried away by the gaseous current, so that frequent renewals of the somewhat costly filtering materials became necessary. Since 1893, part of the cotton-wool has been replaced by cheap fine wood-shavings ("Holzwolle"); in 1896 the washing with sulphuric acid was curtailed, and in 1898 it was entirely abandoned. Since then the moistening of the wool has ceased; it retains its porosity and therewith its efficiency. The gases have since been purified without the assistance of liquids, exclusively in the dry way, and that with such perfection that the contact-substance retains its activity for years. Practically the process is performed as follows:—The gases, as they come from the kilns, are passed through leaden flue-dust tunnels where most of the dust is deposited, afterwards through a set of lead towers, packed successively with coke, charcoal, wood-shavings, and cotton-wool. From the last tower the gas, now absolutely free from dust, is aspirated by the fan-blast and propelled with moderate pressure into the contact-ovens.

4. *The Contact-substance.*—From 1879 to 1883 *platinum asbestos* with 40 to 50 per cent. platinum was used, prepared by means of sodium formiate (p. 1428). In consequence of the impurities at that time still present in the gases, the platinum asbestos soon became inactive, especially by incrustations of sulphates, and had to be frequently worked over again in troublesome manner. In 1883 the transition was made to *platinised pumice*, containing 3 or 4 per cent. platinum, whose activity lasted up to a year. In 1888 this was replaced with excellent results by unglazed *platinised porcelain*.

5. *The Temperature of Combination.*—According to the experiments made at Freiberg, the union of  $\text{SO}_2$  and O is best effected at a temperature of  $440^{\circ}$  to  $460^{\circ}$  C. as measured by a Heracl (Le Chatelier) pyrometer. The inside of the retort-furnace faintly red-hot, but at  $440^{\circ}$  the red sheen ceases. Any effe

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of the heat of reaction upon the temperature could not be noticed.

6. *The Degree of Combination.*—During the first ten years of working the degree of combination attained was imperfect. The  $\text{SO}_2$  percentage of the kiln-gases, originally 7 to 7.5 per cent., was diminished to about 4 per cent.  $\text{SO}_2$ , equal to a conversion of about 45 per cent. into  $\text{SO}_3$ . This did not matter

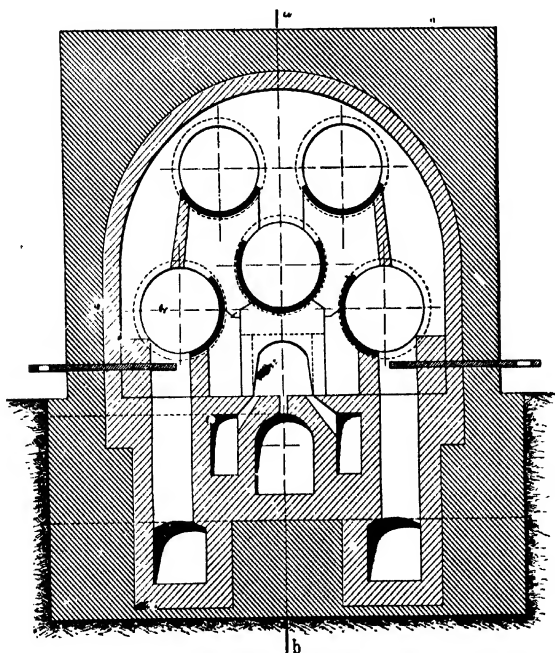


FIG. 512.

much, as the gases were afterwards treated in vitriol-chambers. But already then it was noticed that the gas containing 4 per cent.  $\text{SO}_2$  if sent through a second contact-furnace, came down to 0.2 per cent.  $\text{SO}_2$ , so that in all 97 per cent. was converted into  $\text{SO}_3$ . In 1889 it was noticed that the formation of  $\text{SO}_3$  was increased to 85 or 90 per cent. by one single passage through the contact-substance, if the percentage of oxygen essentially exceeded that of sulphur dioxide; since then gases

with only 6 per cent.  $\text{SO}_2$  have been worked and the uncombined residue of  $\text{SO}_2$  is removed by absorption.

7. *The Contact-furnace.*—The sketches, Figs. 512 and 513, show that each furnace contains five horizontal retorts, charged with contact-substance and heated by means of a gas-producer.

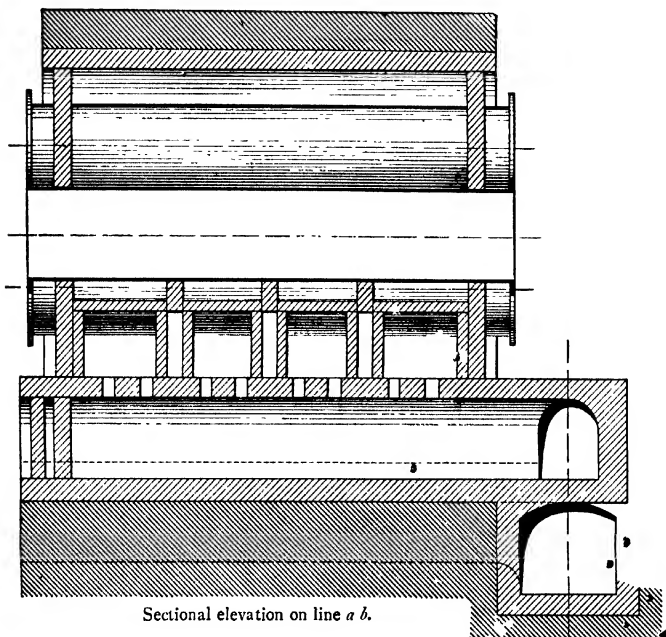


FIG. 513.

Such a furnace yields from 20 to 24 cwt.  $\text{SO}_3$  per twenty-four hours.

8. *The Absorption of the Anhydride.*—The  $\text{SO}_3$  vapours escaping from the contact-retorts under slight pressure are completely absorbed in vertical towers fed with concentrated sulphuric acid, the acid flowing out strongly fuming. It is either sold in this state or is worked for anhydride by distillation in iron retorts.

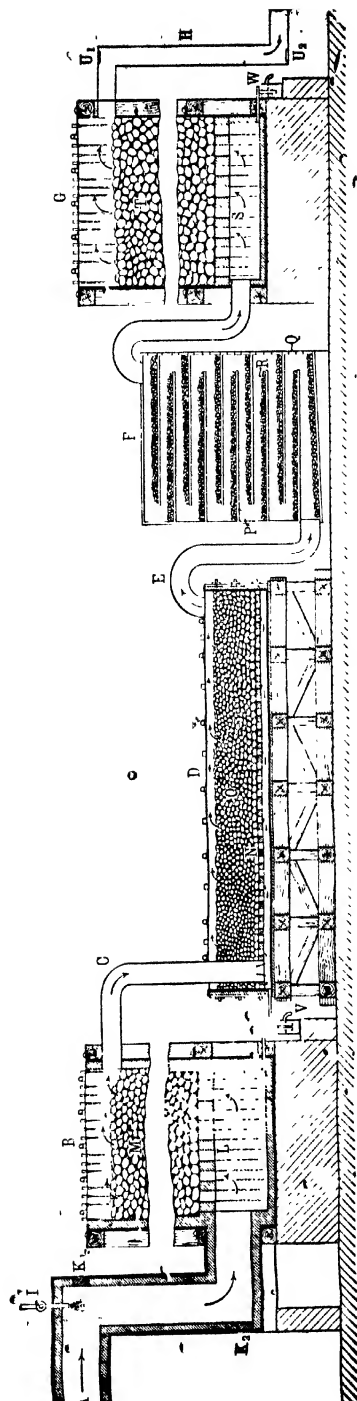


FIG. 514.

VII. *Rabe's Process.*

Concerning Rabe's process for the manufacture of sulphuric anhydride I have received the following communications from the late Mr Niedenfuhr, who has erected several plants on this system, which performs three operations—the purification of the gases, the contact-process, and the absorption of the  $\text{SO}_3$  formed. The purification is described in a Hung. P. 21959 of 12th November 1901. The misty particles contained in the gases must be removed so completely that even after a number of years no deposit is formed on the glass windows interposed in the pipes, and of gaseous admixtures only those must be left which are absolutely harmless.

The hot gases are cooled by direct contact with the cooling-liquid, in two phases. In the first the cooling-effect is carried on up to the point that the liquid completely evaporates; in the second phase so far that the liquid is only heated. This admits of carrying out the cooling-process in a vessel made of an unalterable material, e.g. pottery surrounded on the outside by lead or iron. Such apparatus is not acted upon or stopped up even if the sulphuric acid used for drying has a concentration of  $60^\circ \text{Bé}$ .

The purifying process will be better understood by means of the sketch (Fig. 514).

The gas enters by a cast-iron pipe A, lined with acid-proof material and possessing cleaning-holes  $K_1$  and  $K_2$ . By means of the Kötting's spray-producer I enough water or sulphuric acid is introduced to be completely evaporated. The cooling of the gases thus effected is completed by tower B. This is built like a Glover tower, the bottom and sides being lined with acid-proof pottery; by the grid L the packing M is supported and is moistened by cold strong sulphuric acid, fed in at the top and equally distributed. The hot acid is run out by V into a cooler. The mud is easily collected and no stoppage of the tower takes place.

The cooled gases are now freed from mechanically suspended impurities by filters, consisting of a lead box, D, in which on a grid N the filtering-material O is spread in a thin layer. The latter consists of small pieces of coke, from .10 to 1 mm. diameter, systematically placed so that the coarser grains are

at the bottom, the finer at the top. The filtering-surface must be very considerable in order to avoid loss of draught by friction. The impurities collecting in the filter are removed from time to time by rinsing.

In lieu of the finest grain of coke, fibrous materials may be employed, *e.g.* asbestos, which is prevented from being compressed by being spread on several sieves adjoining each other.

By the filtering-processes the gases are rendered absolutely transparent, which is constantly controlled by means of glass sights; but they still contain gaseous impurities. Only the constituents of atmospheric air—oxygen, nitrogen, carbon dioxide, argon, etc.—are harmless; all other gases (besides  $\text{SO}_2$ ) must be removed. Rabe has found that hydrogen chloride occurs in roasting-gases, and that it can be removed by sodium bisulphate in concentrated solution or in pieces. This takes place in box F, with shelves P and purifying-material R.

The gases are now dried in the acid-fed tower G, containing a packing T on grid S, and pass through pipe II, provided with glass-sights  $U_1$  and  $U_2$ , into the contact-apparatus (not shown!). W is the hydraulic seal for the acid running out of G.

Rabe considers as special advantages of his purifying-process: the possibility of working with natural draught, the complete drying of the gases, the removal of the misty particles without the use of a washing-process, and therefore but slight expense for maintenance and supervision.

(The same advantages are claimed by Rabe for producing acid free from iron and arsenic when made by the lead-chamber process, in lieu of acid made from brimstone.)

Concerning the contact-process itself, Dr Rabe gives me the following notes:—The purified and dried gases are brought into contact with the catalyser in comparatively wide chambers, where the mass is spread on sieves, between which loose sieves can be interposed. This arrangement is preferable to placing the contact-mass in narrow tubes, as the mass can thus be spread more uniformly, which can be controlled at sight, and as the gases are always mixed over again after having passed through a layer of contact-substance, so that any unequalities in the temperature and composition are removed. It is also possible by this means to carry out the reaction in different phases, by employing different contact-masses, or different

temperatures, or combinations of both. In order to produce the proper temperatures, various means can be employed. Thus, according to the Ger. P. 143593 "regulating"-tubes can be placed in the contact-chamber, or as bearers for the contact-sieves, which communicate their temperature to the contact-mass. Wide contact-chambers also produce the least resistance to the propulsion of the gases.

The degree of conversion of  $\text{SO}_2$  into  $\text{SO}_3$  is most easily calculated from the analysis of the gases before entering and after leaving the contact by Reich's method (*suprà*, p. 571). If, for instance, 10 c.c. decinormal iodine solution is employed for each test, corresponding to about 12 c.c. gaseous  $\text{SO}_2$  at ordinary temperatures, and if before entering the chamber the water run out of the aspirator had been = 150 c.c., but after leaving the chamber = 3000 c.c., the degree of conversion is:

$$\frac{(3000 - 150)}{3000 - 6} \times 100 = 95.2 \text{ per cent.}$$

If for the second test another quantity of iodine solution had been used, a corresponding correction must be made.

In order to properly absorb the  $\text{SO}_3$  by concentrated sulphuric acid, the latter must be kept cool, which Rabe effects by specially constructed "reaction-towers" with surface-feeding.

In *Z. angew. Chem.*, 1900, p. 960, Niedenführ mentions that the total fuel required for producing 100 parts  $\text{SO}_3$  is 20 kg. coal. The supervision of the process is very simple, and is facilitated by automatic apparatus on the principle of Rabe's measuring-process for gases and liquids (Ger. P's. 111019 and 112835).

The B. P. of Rabe, 3327 of 1901, substantially agrees with the preceding description, but we shall quote the claims verbatim. The hot gases are preliminarily cooled in conduits with neutral walls, by means of vaporising water or sulphuric acid, to a temperature at which there is not yet condensation of fluid matters, then cooled to a temperature of less than  $100^\circ \text{C}$ . by direct contact with sulphuric acid of any preferred strength in towers not too closely packed, and conducted systematically through filtering-layers of granular substance gradually reduced in size, or of fibrous character, until, when in a dry state, they leave no efflorescence on the glass of the Tyndall testing



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apparatus even after a long time, and then, after being entirely freed from any non-neutral gaseous elements by means of suitable reagents (as, for instance, from muriatic acid by means of bisulphites in a solid form or in the form of a concentrated solution), they are dried in the usual manner.

Dr Rabe informs me that his process has been introduced for manufacturing sulphuric anhydride from pyrites-lumps and fines and from zinc-blende. The following results have been obtained at one of these places during a prolonged period of work. Cost of 100 kg. sulphuric anhydride:—

	Marks.
96 kg. pyrites 43 per cent. S at 1.80 M. . . . .	1.73
10 „ coals at 2 M. . . . .	0.20
2.4 H.P. hours for moving gases and acid at 0.05 M.	
per electrical H.P. . . . .	0.12
0.16 shift at 2.50 M. per man and shift . . . . .	0.40
Repairs . . . . .	0.32
	2.77
Sinking fund for plant, costing 130,000 M. per 5000 kg.	
per day, equal per 100 kg. to . . . . .	0.87
Total . . . . .	3.64

(The cost of 130,000 M. for a plant for the daily production of 5000 kg.  $\text{SO}_3$  does not include royalty, and is decidedly less than will be required in most places for a substantially constructed plant.—G. I.)

### *Notes on the Development of the Contact-process in the United States.*

The following notes have been supplied to me by a leading firm in the American chemical industry, and have been first published by me in *Z. angew. Chem.*, 1910, p. 721:—

“The first successful introduction into the United States of the catalytic process for manufacturing sulphuric acid took place in the year 1898, when the Badische Anilin- und Sodafabrik erected an experimental plant, constructed according to the Knetsch inventions, in the State of New Jersey, and there demonstrated the immense importance and value of his ideas. From this demonstration as a starting point, and the subsequent acquisition of the Knetsch patents by the General Chemical

Company, the contact-system reached its present extensive development in the United States.

"A year later, that is in 1899, the Mineral Point Zinc Company erected an apparatus at their works in Wisconsin under the patents of Schröder and Grillo. It was designed to utilise the sulphurous gases from the non-arsenical fumes of zinc ore previously wasted; but the detail and full requirements of the contact-system not being at that time generally understood, it is not surprising that this plant was rebuilt a number of times and finally dismantled.

"The General Chemical Company began the erection of their first plant under the Herreshoff system<sup>1</sup> in 1900, and early in 1902 commenced manufacturing sulphuric acid in their main New York Works. This plant has run continuously since then on the same contact material, the catalytic mass never having been touched. This was the first plant in the United States to use pyrites-burner gases containing arsenic and other impurities.

"One of the Herreshoff patents in 1904 came into interference with a Knietzsch patent owned by the Badische Anilin- und Soda-fabrik. As a result of the proceedings that followed, the Badische and the General Chemical Company joined forces, the General acquiring all of the patents owned by the Badische, and later the patents of the Farbwerke Meister, Lucius and Brüning the Tentelewische Chemische Fabrik, and Rabe.

"The General Chemical Company is said to have practically dismantled its chamber-acid plants throughout the United States since 1903, substituting contact-plants almost entirely for the old chamber and concentrating systems. The other chemical companies using the contact-process, with few exceptions, are their licensees.

"The Herreshoff inventions as applied to those of Knietzsch resulted naturally in material improvements, in the elimination of needless and expensive compressors, in the avoidance of the gas immersion in liquid, and in a changed arrangement for heat regulation by removing the heat of reaction in separate heat transferers and not within the contact-chamber. These systems have been so efficient, that it is said that converters which have been in continuous or nearly continuous operation for nine years have never been opened, and are still working a

<sup>1</sup> Vide p. 1425.

actively as ever. In the matter of absorption, too, improvements have been introduced by the combined inventive activity of Messrs Knietsch and Herreshoff, whereby the strength of the acids is kept constant by means of continuous circulation of large volumes of acid, thereby also reducing the pressure formerly required at this point to almost zero.

"The New Jersey Zinc Company owns the Schröder-Grillo process for the United States. Besides their own use of this process on zinc ores they have granted a few licenses to other parties in the United States. It was claimed by those holding the Knietsch patents that this, like all other workable contact-processes, infringed certain basic inventions of the Knietsch process. Suits were brought, but a compromise was effected, leaving the Herreshoff-Knietsch patents supreme in the future growth of the chemical field."

According to Quincke (*Z. angew. Chem.*, 1910, p. 1923), most of the sulphuric anhydride in the United States is manufactured in the numerous factories of the General Chemical Company, according to the system of Herreshoff which substantially agrees with the apparatus of Knietsch. The Mannheim process is worked by the Grasselli Chemical Company, Schöllkopf, Hartford Hanna in Buffalo, and the Dupont Powder Company. The Schröder-Grillo process is also worked by a number of factories, and the Tentelew apparatus by the Merrimac Chemical Company. About one-quarter of the sulphuric acid manufactured in the United States is made by contact-processes; the total production of sulphuric acid in that country amounts to  $1\frac{1}{2}$  million tons per annum.

The contact-processes have also been tried for dealing with the acid fumes of the Tennessee copper works, but unsuccessfully. That aim has been attained only by the introduction of enormous lead-chamber plants (*Chem. Zeit. Rep.*, 1910, p. 372).

According to the English Alkali Inspectors' Reports for 1909 the manufacture of sulphuric acid by contact-processes in the United Kingdom was then still in the experimental stage (which statement cannot be accepted in the face of the information just given).

*A. Purification or Special Preparation of the Pyrites-burner Gases for the Manufacture of Sulphur Trioxide.*

In this place we enumerate only those processes which have not been previously mentioned in the description of various processes for the manufacture of  $\text{SO}_3$ .

Raynaud and Pierron (B. P. 16283 of 15th February 1900) purify the gases, first by condensing or compressing the gases, and then allowing expansion to occur. They prefer condensing the gases by absorbing them in kieselguhr, and expanding them by raising the temperature after a certain interval. The impurities are said to remain behind in the porous material, which must be from time to time renewed.

H. Howard (Amer. P. 801318) reheats the gases, after they have been cooled by the process of purification, by means of U-shaped pipes, placed in the pockets of a special chamber, before they enter the contact-apparatus.

Th. Meyer, in *Z. angew. Chem.*, 1906, pp. 1313 to 1319, discusses at length the processes for the filtration of gases, in order to free them from dusty particles and from sulphuric acid in the shape of mist, etc., and he describes a filter employed by himself, in which there is a number of layers of gravel and sand of various degrees of fineness. He recommends it not merely for the gases in the anhydride process, but more especially for exit-gases from the manufacture of all acids. It is supplied by the Deutsche Ton- und Steinzeugwerke, Charlottenburg.

Messel (B. P. 22672 of 1909), in order to increase the yield of sulphuric anhydride or sulphuric acid, passes gases containing  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  over granulated gas coke, maintained at a temperature of about  $425^\circ$ . His Ger. P. is 226331.

The same process is described in the Fr. P. 414387 of the Badische Anilin- und Sodafabrik, where it is stated that thereby the  $\text{SO}_3$  is taken out of the gases by transforming it into  $\text{SO}_2$ , by means of heating the gases in the presence of a reducing substance, e.g. coke, to  $425^\circ$ . The removal of the already existing  $\text{SO}_3$  from the burner-gases increases the catalytical production of fresh  $\text{SO}_3$  and renders the purification of the gases easier; the  $\text{SO}_3$  fumes, by forming a fog of sulphuric acid, enclose and carry forward the contact-poisons.

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Hegeler and Heinz (Amer. P. 931868) mix the burner-gases with a portion of the gases obtained during the process and already cooled, at least up to the boiling-point of the washing-fluid; they then pass through a washer, fed with dilute sulphuric acid, a cooler, a drier, a preheater and the contact-furnace. The gas intended for mixing with burner-gas is drawn out by a fan behind the cooler.

Rahtjen (Ger. P. 226107) mixes gases containing  $\text{NH}_3$  (from the destructive distillation of organic substances) with pyrites-burner gases and then treats them in the usual manner for the production of ammonium sulphate, whereby  $\text{SO}_2$  remains in a state of purity such as is required for the manufacture of  $\text{SO}_3$  by the contact-process.

Blackmore (Amer. P. 769585) during the action of  $\text{SO}_2$  and O introduces fresh portions of the gaseous mixture, in order to prevent overheating.

H. A. Frasch (Amer. P. 715778 of 16th December 1902) obtains sulphur dioxide in a concentrated condition, suitable for the manufacture of sulphuric acid or anhydride by the contact-process, as follows:—The pyrites-burner gases are washed and cooled and subjected to pressure in contact with water already saturated with  $\text{SO}_2$  at atmospheric pressure; they are then washed under pressure with fresh water, and the surcharged solution is reduced to atmospheric pressure, the gas evolved being stored or at once utilised. The surplus solution is heated, and the  $\text{SO}_2$  evolved is returned to the absorber.

### *Purification of the Burner-gases from Arsenic.*

The removal of arsenic from the burner-gases, in which it is present in the shape of arsenious oxide,  $\text{As}_2\text{O}_3$ , takes place incidentally in all ordinary processes for purifying those gases, described, e.g., in Chapter IV., *supra*, pp. 555 and 1415, but not completely. The complete or nearly complete removal of the arsenic is of course an advantage in the manufacture of ordinary sulphuric acid, but it is stated by various inventors to be quite essential in the manufacture of sulphuric anhydride,  $\text{SO}_3$ .

We now enumerate the various proposals for taking the arsenic completely out of pyrites-burner gases, as far as they

have not yet been mentioned before in connection with the description of processes for manufacturing  $\text{SO}_3$ .

Projahn (Ger. P. 221847) passes the burner-gases through porous anhydrous aluminium sulphate obtained by heating hydrated aluminium sulphate, which retains nearly all the arsenic contained in the gases (see above).

Stone (U.S. Ps. 711187 and 711188) cools the gases down to such a temperature that the arsenic is precipitated, whereupon it is removed by filtration. The filtering-substance is later on heated, whereby the arsenic is driven out and is condensed.

Duron and Hartmann (B. P. 9869 of 1910; Fr. P. 415658) filter the burner-gases first through a layer of ferric sulphate or the like, to remove the coarsest impurities and most of the arsenic, and then treat them in a series of chambers with sprayed sulphuric acid; thus cooled to 100 to 150°, the gases pass up a tower, fed with water, then through filters filled with quartz or coke and then through reheaters, before being used in lead chambers or in the contact-process. In the first stage of the process the gases are enriched by  $\text{SO}_2$ , produced by the decomposition of  $\text{SO}_3$  from the ferric sulphate; any ferric oxide thus formed and carried along by the gases is reconverted into ferric sulphate by treatment with sulphuric acid.

According to Reese and the Du Pont de Nemours Powder Company (U.S. P. 989801) the impurities of pyrites-burner gas, which are injurious to the contact-processes for making  $\text{SO}_3$ , such as arsenic, lead, chlorine, and fluorine compounds, as well as sulphuric-acid fog, are completely retained by passing the gases (previously purified from flue-dust, cooled, washed, and dried) through a filter containing *dry*  $\text{CaO}$ , or  $\text{Ca(OH)}_2$ , or  $\text{CaCO}_3$ , or dolomite, kept below 54°. In this case the  $\text{SO}_2$  is not retained by the  $\text{CaO}$ , nor is there any formation of sulphite or bisulphite.

#### B. *Special Contact-apparatus and Regulation of Temperature.*

Remmert (Ger. P. 59556 of 1890) laid down the principle that when hot gases are passed over solid substances whereby they undergo a change with development of heat, layers of different temperature are produced at right angles to the

direction of the gaseous current. This holds good also in the formation of  $\text{SO}_3$  by the contact-process. The gases, getting heated by this process, raise the temperature of the following layers of the contact-substance to the point of reaction. Thus the reaction spreads over the whole mass, but the heat of the gases going out is lost. This can be avoided by reversing the direction of the gaseous current, when the heat is at a maximum at the far end of the contact-apparatus, and introducing the gases first at that end. This causes a more equal temperature and a saving of fuel in the previous heating of the gases.

Raynaud and Pierron (B. P. 16254 of 1900) improve the catalytic action in one of the following ways:—First, the temperature is kept uniform, but the contact-substance used is first poor in platinum, then rich, and then again poor; second, the contact-substance remains the same, but the temperature is first low, then higher, then again lower. During the first phase the reaction  $\text{SO}_2 + \text{O}$  is commenced, during the second phase it is completed; but as there is again a dissociation of  $\text{SO}_3$ , this is brought back in the third phase.

Babatz (B. P. 1216 of 1900) heats the purified kiln-gas by the non-purified gases on their way to the purifying-plant. The heat obtainable from this source should be more than sufficient for bringing up the purified gases to such a temperature that no further heating of the contact-apparatus is required (cf. *supra* the previous patents of the Badische and of Höchst).

Daub and Deuther (B. P. 9536 of 1902) try to prevent the overheating of the contact-substance by the reaction-heat in the following manner:—The apparatus consists of alternately arranged heating- and contact-chambers, the former being provided with independent means for heating or cooling the gases, and the latter with a passage for the whole of the gas conducted into the apparatus through contact-material disposed in the contact-chamber in such a manner that the gases and contact-matter reciprocally maintain and equalise the temperature in the chamber and prevent local overheating.

P. Naef has taken a number of patents concerning a method of treating solid materials with gases, consisting in passing no gases through the solid material, withdrawing, readjusting the

temperature, and repassing the gas through the solid material so as to simultaneously produce several gas-circuits through the solid material. In one of these (B. P. 23415 of 1899) he brings in the oxidation of  $\text{HCl}$  or  $\text{SO}_2$  by air. Other patents follow in 1900, 18188 with 134 claims, 18191 with 154 claims; then 14977 of 1901.

Wenmaekers (B. P. 19902 of 1901) passes the gases from pyrites-kilns through cooling-pipes, then through a dry coke-tower, thence to another tower into which steam is injected, and lastly through a coke-tower sprayed with concentrated sulphuric acid. From here they pass into the contact-apparatus, the heat of the issuing gases serving to heat up the arriving gases. After taking out the sulphuric anhydride formed, the gases, still retaining  $\text{SO}_2$ , are returned to the steaming-column and re-enter the process.

Stone (Amer. P. 711186) describes a contact-apparatus consisting of independent sections, each containing an individual

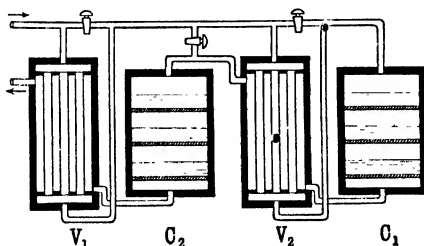


FIG. 515.

charge of contact-substance. Each section, as its charge becomes spent in working, is replaced by a freshly charged section.

Herreshoff (Amer. Ps. 719332 and 719333) effects a partial conversion of the gases into  $\text{SO}_3$ , then cools the residual gases by heat exchange with entering gases, and returns them to the contact-apparatus for complete transformation. For this he employs a specially constructed apparatus, as shown in Fig. 515. Quincke calls it, "a Knietsch contact-apparatus, drawn asunder"; it is used by the General Chemical Company (*suprà*, p. 1419). The following Amer. Ps. of Herreshoff contain details on his system: 722981, 737625, 723595,



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737233, 737626, all of 1903; 940595 and 940596 of 1909; 955067 and 969868 of 1910. *Vide supra*, p. 1419.

Ferguson (B. P. 6824 of 24th March 1903; Amer. Ps. 723595 and 723596) employs two contact-chambers; after the gases have passed the first, and have been partially converted into  $\text{SO}_2$ , more air is mixed with these, and they are now passed through the second chamber, where the conversion is completed.

Sébillot (B. P. 21616 of 1898; Amer. P. 700249) makes sulphuric acid (*not* anhydride) by burning sulphur-ores in a "blast-furnace" in which ore and fuel are alternately charged, air being forced in. The gases pass into a mixing-chamber, and from this into contact-chambers. These contain, on a perforated bottom, pieces of pumice-stone, the interstices being filled with loose asbestos, and above this a series of perforated stoneware plates, each supporting a layer of asbestos and of spongy platinum. Into the free space above, the hot mixture of sulphur dioxide and air is led along with steam and a regulated supply of air, and the gaseous mixture is drawn down through the contact-material into the bottom chamber of the column, in which pipes are set, cooled by a current of water, whereby the acid-vapours are condensed.

Lc Blanc and Krauss (Amer. P. 726076 of 1903) pass gases, containing about 7 per cent.  $\text{SO}_2$  and 9 per cent. O, into a first contact-chamber, kept at about  $500^\circ\text{C}$ ., in the proportion of about 102 l. of burner-gas to 1 kg. platinised asbestos per minute, and afterwards at the same speed through a second chamber kept at about  $400^\circ\text{C}$ .

Blackmore (B. P. 27907 of 1904) seeks to prevent an injurious rise of temperature in the combination of  $\text{SO}_2$  with O by abstracting the heat through the simultaneous production of a substance which absorbs heat on its formation. The specification contains forty-one claims, and should be consulted in the original. For the same purpose the same inventor also makes use of the nitrogen oxides for transferring O upon  $\text{SO}_2$ ; *vide* his Amer. Ps. 778099, 828268 and 769585, *supra*, p. 1422.

Ferguson (Amer. P. 857389) constructs his contact-chamber in the form of a long, upright tube with perforated shelves, on which the contact-substance is placed. The outside is

furnished with ribs between which asbestos or similar material is placed, or channels for the passage of heated air are arranged there.

Babatz-Rheingöntheim (Ger. P. appl. R43062) interposes a cooling-space between two contact-chambers, the cooling medium being air, passed through in pipes. This equalises the temperatures in the contact-spaces, and produces better yields.

Sébillot and Monclaire (B. P. 2192 of 1909; Fr. P. 386672) employ very dilute  $\text{SO}_2$  gases from roasting furnaces, which they pass into the top of a fire-brick chamber, with perforated shelves, covered with asbestos cloth, on which rests the catalytic material (ferric oxide, asbestos fibres, pumice, etc.).

Wischin (B. P. 12419 of 1903) passes  $\text{SO}_2 + \text{O}$  (or air) through an annular section containing contact-material, the outside of which section is exposed to a cooling atmosphere, and then through a similarly packed wider annular section, enveloped by the first section, with or without an intervening space. No external source of heat is needed; only the gases are admitted in a hot state.

M. Neumann (Ger. P. 187077) by his invention tends to compel the gaseous current to spread at once equally through the contact-apparatus, in which, he says, otherwise only one-third of the contact-mass exerts its full action, while by his new arrangement an apparatus, built for 6 tons, will furnish 18 tons. For this purpose he places in the centre of each layer round the axis a quantity of the finest contact-substance, offering the greatest resistance to the gases; then follows concentrically a layer of coarser, less densely lying material, and so forth, the coarsest material being at the periphery. This is effected by arranging concentric sheet-iron cylinders, open at top and bottom, on the bearing-sieves. A cooling-pipe passes through the centre, through which cooling-air passes in at the bottom and out at the top, without getting mixed with the gases.

Kauffmann (B. P. 7074 of 1904) performs the first part of the conversion of  $\text{SO}_2 + \text{O}$  into  $\text{SO}_3$  at a higher temperature than the second part, which takes place in a chamber provided with a cooling-arrangement.

The Nordyke & Marmon Company (B. P. 1204 of 1906) describe a helical catalytic chamber of a metal of the platinum

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group through which the fluid to be treated may be passed at any suitable pressure and in which, after it has been preliminarily heated, both endothermic and exothermic compounds are formed serving to balance thermally and to maintain the desired temperature.

### *C. Improvements in the Manufacture of Contact-substances, Platinum, etc.*

It may be assumed that 1 kg. platinum, in the shape of ordinary platinum asbestos, can produce with a good process from 600 to 700 kgs.  $\text{SO}_3$  per twenty-four hours. The high price of platinum makes it desirable to prepare very active contact-substances.

A Ger. P. of Cl. Winkler's (4566 of 21st September 1878) describes the preparation of extremely active catalytical substances from precious metals or metallic oxides in the finest state of division, with which an indifferent porous matter is impregnated almost in the same way as a textile fabric is dyed in the beck. The best catalytical substance is platinum, also iridium or palladium, less so the oxides of iron, chromium, manganese, cobalt, and copper. As an indifferent menstruum almost any loose porous substance may be used, preferably asbestos, but also glass-wool, pumice, infusorial earth (kieselguhr), clay, and where a very high temperature is not required, even cellulose, cotton-wool, gun-cotton, sponges, etc.

In order to charge asbestos with finely divided platinum, it is thoroughly soaked with a solution of platinum chloride made alkaline by soda and mixed with sufficient sodium formiate to reduce the platinum. The well-wrought pasty mixture is dried in a water-bath; thus the platinum is separated as "platinum black," and is firmly precipitated upon the fibre. The salts are removed by washing, without washing off the platinum. The quantity of the latter precipitated depends upon the strength of the solution of platinum chlorides; with asbestos or cotton-wool a percentage of 80 platinum may be attained. Metallic oxides exhibit catalytical action only at higher temperatures, and, accordingly, must be precipitated upon fire-proof substances. Thus asbestos or pumice may be thoroughly impregnated with chromium oxide by soaking in mercurous nitrate, then in

ammonium chromate, drying each time, and ultimately gently igniting. Cupric oxide is precipitated firmly by soaking in an ammoniacal solution of cupric carbonate and gently igniting. Asbestos may also be soaked with solutions of manganous or cobaltous chloride, etc., dried, put into a heated solution of bleaching-powder or of another precipitant, dried again, washed, and ignited. The contact-substances prepared in this way, owing to their homogeneous condition and their very large surface, cause, either at the ordinary or at a higher temperature, the combination of certain gases, such as that of  $\text{SO}_2$  and  $\text{O}$  into  $\text{SO}_3$ , the conversion of the  $\text{CS}_2$  in coal-gas into  $\text{H}_2\text{S}$ , the oxidation of the vapour of alcohol, etc. They may be employed for all reactions based upon the phenomena of so-called "catalytic action."

*The preparation of extremely active platinum black* has been described by Loew (*Ber.*, 1890, p. 289). Already Doebereiner has shown that the degree of activity of platinum black differs very much with the method of preparation employed. That made with zinc and hydrochloric acid is less active than that made with an alkaline solution of glucose, and this is inferior to that which is precipitated from platinic sulphate by alcohol. The proportion is 1 : 1.8 : 2.6. Far more active again is the following preparation, made with formaldehyde of 40 or 45 per cent.:—50 g. platinic chloride are dissolved in a little water, to a vol. of 50 or 60 c.c., and mixed with 70 c.c. of 40 to 45 per cent. formaldehyde. To this is added, quite gradually and with good cooling, a solution of 50 g. caustic soda in the same quantity of water. Most of the metal is separated at once. When, after twelve hours, the mass is filtered by means of a filter-pump, a yellow solution passes through, which on boiling separates a little metal. When, however, most of the salts (sodium chloride and formate) have been removed by washing, a deeply black solution runs off, some of the black mud going into solution. Therefore the washing is interrupted until an oxidising process now going on in the black mud has been finished, whereupon the liquor runs off colourless. That process consists in the rapid absorption of oxygen by the black mass on the filter; the temperature rises to  $36^\circ$  or  $40^\circ$ , and many gas-bubbles are given off with a crackling noise, lasting for several hours. The fine mud has now turned into a loose porous mass.

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which is washed till every trace of chlorides has been removed, then pressed and dried over sulphuric acid.' Even a trace of sodium chloride is extremely prejudicial to the action of the platinum black, a coating of platinous chlorine being formed in that case. The black mass evidently contains an organic compound of platinum, which is afterwards destroyed by oxidation.

Majert (Ger. P. 134928) dissolves platinum chloride in ethyl alcohol, methyl alcohol, acetone, or acetic ether, soaks asbestos or the like in that solution, and sets fire to it. The platinum is reduced to the metallic form in a very fine state of division, and firmly attached to the asbestos. Thus platinised asbestos of great efficacy can be obtained with only 2 per cent. platinum.

Langhans (Ger. P. 134738) employs the double compounds of methyl sulphide or its homologues with the halogen compounds of platinum dissolved in bromoform.

Klaudy and Efrem (B. P. 14339 of 1899) employ as usual a fire-proof carrier, with a platinum salt and an organic reducing-substance, but together with hydrofluoric or hydrofluosilicic acid. They employ meerschaum or clay, which is treated with aqua regia or strong sulphuric acid, and freed from the soluble salts thus formed by washing with water. They then add the platinum salt and a reducing-agent, such as sugar, with or without finely divided carbon, and, moreover, hydrofluoric or (preferably) hydrofluosilicic acid, the latter for the purpose of forming a hard porous mass, which especially acts also by etching the smallest particles of the clay and enlarging the active surfaces. The paste thus formed is moulded, dried, and ignited. These masses act as catalysts already at ordinary temperatures, especially for lighting gas-flames, and are much harder and more durable than platinised asbestos, etc.

Goldenberg, G6romont, & Company (B. P. 618 of 1900) prepare contact-substances from non-porous sintered materials in the shape of spheres, cylinders, or plates, on which a very thin porous layer of clay has been fixed by burning. Both materials must be heat- and acid-resisting. These bodies are treated with platinum solution, which penetrates only through the porous surface, leaving the sintered cores free, so that the platinum is fully utilised by the gases circulating between the bodies which diffuse through the thin layer.

Saubermann (Ger. P. 125988) divided the asbestos into fine parallel fibres, which are spun into tissues (principally for incandescent mantles).

Carey, Heslop, and the United Alkali Company (B. P. 10351 of 1902) precipitate platinum upon inorganic salts (sulphate of soda). In this case any acid and aqueous particles contained in the gases are said to do no harm.

Neuendorf (Ger. P. 127846 of 28th October 1899) evaporates a solution of barium (strontium or calcium) chloride to dryness, impregnates the dry crusts formed with a solution of platinum chloride, dries the mass, and converts it into sulphate by a stream of  $\text{SO}_2$ , steam, and air, or by vapours of  $\text{H}_2\text{SO}_4$  at a high temperature. Or, preferably, he first forms the sulphate in the aforesaid manner, and subsequently soaks it with platinum chloride.

Porter (Amer. P. 612614 of 18th October 1898) describes (principally for use in lighting gas-jets) mixtures of a catalytical metal (platinum, etc.) with infusible metallic oxides (mainly  $\text{Al}_2\text{O}_3$ , but also the oxides of Zr, Ce, Mg, etc.) produced as follows:—A solution of 1 part platinum chloride is mixed with 8 parts hydrated aluminium chloride and the mixture is used for impregnating cotton, wood-pulp, or other combustible materials. This product is heated in contact with air, the organic substance is burnt and leaves behind a mixture of metallic platinum and alumina in a very porous form. The organic substance causes the reduction of Pt at a low temperature, and the alumina prevents the platinum black from uniting into a denser form. Preferably 1 part Pt is employed to 2 to 6 parts Al.

Schick (Amer. P. 971149) reduces platinum from solutions on surfaces of quartzite or porcelain, and fixes it by heating up to  $1400^\circ$ , so that it softens.

O. Niedenführ (Ger. P. 225705) produces contact bodies by precipitating platinum on a hollow metallic body, either electrically or chemically, inside or outside, or on both faces. The metallic body is made preferably of cast-iron, but Cu, Zn, or Al may also be employed. Such metallic bodies are preferable to those made of earthenware, porcelain, or asbestos, because, owing to their good heat-conducting power, the reaction space can be easily kept at a uniform temperature.

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Neumann (Ger. P. 188503) employs somewhat dense carriers, e.g. produced by first treating with water-glass and then with hydrofluosilicic acid, or with  $\text{BaCl}_2$  and thereupon with  $\text{H}_2\text{SO}_4$ , for the platinum contact-mass, which are first treated with a reducing solution, and then at a higher temperature with an alkaline solution of platinum chloride; the latter is at once reduced to metallic Pt, spread on a very large surface. His Ger. P. 218725 provides for stopping up the pores of the underlying bodies by producing a precipitate in them, before proceeding to the platinising-process.

### *Recovery of Platinum from Spent Contact-masses.*

The Badische Anilin- und Sodafabrik (Ger. P. 148196) treat platinum contact-masses which have become inactive with dry sulphur dioxide at the temperature of the contact-process. The  $\text{SO}_2$  is employed either in the pure state or in the shape of roaster gases, containing much  $\text{SO}_2$  and little O. By this means, without introducing any foreign substance, the damage caused by the retention of arsenic in the contact-mass is remedied.

The quantitative recovery of the platinum from inactive platinum asbestos, according to a Ger. P. of the Farbenfabriken Elberfeld, is brought about by treating the asbestos with a mixture of damp chlorine and HCl, lixiviating the  $\text{PtCl}_4$ , precipitating it as potassium or ammonium platinum chloride, and reducing this by sodium formiate.

### *Ferric Oxide (and Similar Oxides) as Catalytic Agents.*

We have in quite a number of cases met with the employment of ferric oxide and other sesquioxides (of chromium, etc.) as catalytic agents for the combination of  $\text{SO}_2$  and O. The theory of this process has been given *suprà*, pp. 1301 *et seq.* We now mention the more recent proposals in that direction.

I have myself contributed to the elucidation of this subject; I found that the quantity of  $\text{SO}_3$  in the burner-gas would be considerably increased by passing the gas through a layer of red-hot pyrites-cinders, i.e. ferric oxide (*Berl. Ber.*, 1878, x. p. 1824, and *Chem. Zeit.*, 1883, p. 29). I then got up to a conversion of 18 per cent. of the  $\text{SO}_2$  into  $\text{SO}_3$  and I did not

pursue the subject any further, because my professed object was attained—viz., to study the process going on in the pyrites-kilns, and to explain the formation of  $\text{SO}_3$  therein—and it did not strike me that, by increasing the duration of the action, a process for making  $\text{SO}_3$  on a large scale might be worked out on that foundation. This was perhaps detrimental to my interests, but I certainly do not deserve the accusation brought against me in the Ger. P. 107995, that I had declared the question of the applicability of ferric oxide as contact-substance for making  $\text{SO}_3$  on the large scale as settled in the negative by my experiments, and that I had thereby misled other inquirers. In *Z. angew. Chem.*, 1900, p. 80, I have disproved this assertion, and those concerned have never said anything more about it. On the contrary, it is clear that my publications had indeed induced others to follow up the subject in various directions, as we shall have to describe in the proper places.

Briegleb (Ger. P. 121906 of 25th January 1900; B. P. 11792 of 18th June 1901) moulds the oxides of iron, copper, or chromium with 10 per cent. clay into briquettes, places them on a grate in an upright shaft, and heats them by means of a second, lower grate, on which coke, anthracite, or charcoal, free from hydrogen, are burnt, or else by producer-gas. The fuel must be free from hydrogen. [Such a fuel, whether solid, liquid, or gaseous, is not known, nor is the heating of the contact-substance at all necessary, as the heat of the burner-gas is quite sufficient for this purpose.]

Blackmore (Amer. P. 686021 of 1901) passes hot sulphur dioxide containing vapours of sulphur over ferric oxide in order to produce  $\text{SO}_3$ , on the principle of replacing the oxygen of ferric oxide by a substance possessing greater affinity to the metal [?]

The same (Amer. P. 686022) brings  $\text{SO}_2$  into contact with  $\text{Fe}_2\text{O}_3$  at a temperature lying below the dissociation point of  $\text{SO}_3$ , passes the  $\text{SO}_3$  formed into a condensing-apparatus, raises the temperature of the iron residue, passes oxygen over it, allows to cool down to a suitable point, and recommences the operation by admitting  $\text{SO}_2$ .

Hans A. Frasch (Amer. P. 664634 of 1900) passes the gases from ordinary ore-burners into a "converter" in which some more sulphur-ore (preferably pyrites) is contained, but only



enough ore is burned therein to maintain the proper temperature and to produce fresh ferric oxide. The gases pass through this catalytic converter from the top downward; there may be a magazine provided for self-feeding, so that the amount of cinders drawn from the bottom regulates the charge of fresh ore and hence the temperature. If necessary, the gases coming from the ordinary roasting-furnace (pyrites-kiln, etc.) can be cooled before entering the catalytic converter, the temperature of the contact-mass being regulated by adjusting the proportions of sulphur burning in, and the  $\text{SO}_2$  gases admitted to the converter. Such a catalytic converter, burning a moderate quantity of pyrites, may be added to the ordinary burners used in the metallurgy of zinc, copper, nickel, etc.

Pyrites-cinders, freshly roasted and charged with ferric sulphate, are employed as contact substance for the manufacture of sulphuric acid or anhydride by Hilbert and the Bayrische Aktiengesellschaft Heufeld (Ger. P. 163835). The cinders, prepared as above, are gradually passed through a shaft, in which pyrites-burner gases ascend. From time to time a quantity of cinders is drawn out at the bottom, and is at once soaked with sulphuric acid, thus forming a layer of ferric sulphate on the surface which greatly assists the effect of contact. This mass is again charged at the top, and gradually, on descending, gets into a zone of such a high temperature that the ferric sulphate splits up into  $\text{SO}_3$  and  $\text{Fe}_2\text{O}_3$ . The latter, being in a state of very fine division, is a much more efficient catalytic substance than the warm ferric oxide formed in the roasting process.

The same parties (Ger. P. 179588) later on effect the production of  $\text{SO}_3$  through the catalytic action of freshly roasted pyrites-cinders in a shaft, built below the pyrites-burner, through which the gases travel from the bottom upwards, thus giving up a portion of their heat to the bottom part of the cinders, and finding the most suitable temperature in all parts of the shaft. The cinders are from time to time partly drawn out at the bottom of the shaft, and this is replenished by fresh cinders from the pyrites-burner above. If the shaft is high enough, all the  $\text{SO}_2$  is transformed into  $\text{SO}_3$  before the gases leave the apparatus.

Wrampelmeier (Amer. P. 948947) converts the pyrites-

cinders into briquettes by moistening them with dilute sulphuric acid, moulding the plastic mass, heating up to the driving off of the water and sulphuric acid and breaking it into pieces (Ger. P. appl. W34092).

Albert and Schulz (Ger. P. 238371) employ mixtures of ferric oxide with the oxides of barium or strontium which, on heating in air or oxygen, are converted into compounds of ferric peroxide with the alkaline earths. These are excellent catalysers for converting  $\text{SO}_2$  into  $\text{SO}_3$ ; at  $450^\circ$  94 per cent.  $\text{SO}_2$  is oxidised in  $\text{SO}_3$ . The contact-action takes place between  $400^\circ$  to  $640^\circ$ ; the optimum is at  $450^\circ$  to  $550^\circ$ . This contact-substance described is not so sensitive against moisture as ferric oxide. The Amer. P. of Albert is 1018402.

L. and P. Wöhler (*Z. physik. Chem.*, lxii. pp. 440 to 453) discuss the dissociation of chromic oxides and cupri-chromic oxides when used as contact-substances for producing  $\text{SO}_3$ .

McFetridge (Amer. P. 988646) injects finely powdered sulphide ore or matte by a blast or suction into a furnace, heated high enough to at once ignite the S, thus decomposing the sulphide into  $\text{SO}_2$  and metallic oxides; the gases produced are carried with air over those oxides, whose catalytic action converts  $\text{SO}_2$  into  $\text{SO}_3$ , the gases thereby being also freed from As.

As contact-substance Projahn (Ger. P. appl. P15803) employs porous *aluminium sulphate*, either by itself or as substratum for a platinum catalyser which is thereby rendered most efficient.

*Chromium oxide* (already employed by Wöhler and Mahla in 1852 and mentioned *suprà*, p. 1281) is proposed for this purpose by Matignon, Trannoy, Urbain, Feige and Varley (B. P. 8102 of 1908; Fr. P. 376629). The oxide is rendered porous, either by calcination of a combination of chromium with a volatile base, such as ammonium bichromate, or by the calcination of chromium nitrate or other chromium salts (other than chrome, alum, chromium sulphate, and chromium chloride), or from the calcination of chromium hydroxide in the presence of a substance which disengages a gas. The masses may be subdivided by any suitable inert material. The best temperature is  $430^\circ$  to  $620^\circ$ .

*Rare Metals and Various Others as Catalysts.*

\* C. J. E. de Haën (B. P. 8545 of 1901; Amer. P. 687834) mixes asbestos with *vanadic acid* in a fine state of division by soaking it with ammonium vanadate and igniting. This reagent is asserted to effect a combination of  $\text{SO}_2$  with O up to 84 per cent. at a temperature of  $465^\circ \text{C}$ . Haeussermann (*Chem. Zeit.*, 1902, p. 6) points out that the vanadium compounds have been known for a long time as oxygen carriers, and have also been proposed for the present case.

Kuster and Franke (*Z. anorg. Chem.*, 1905, p. 453) found vanadium pentoxide very similar to ferric oxide in the catalytic action on  $\text{SO}_2$  and O, but more reliable for a prolonged time.

According to the Fr. P. 318770 of the Company Parisienne de Couleurs d'Aniline, asbestos soaked in *phosphoric acid* and dried transforms 90 per cent. of  $\text{SO}_2$  into  $\text{SO}_3$ .

*Arsenic pentoxide* has been proved to be a catalyser, similar to vanadium pentoxide, ferric oxide, etc., by the above-mentioned investigations of Lunge and Reinhardt and of Berl (*supra*, pp. 1317 and 1318), although  $\text{As}_2\text{O}_3$  in other cases acts as a contact-poison (*Opl. Chem. Zeit.*, 1905, p. 757).

Bonhard and Loyer (Fr. P. 321573 of 1902) employ the oxides of metals of the *tantalum* group, after reducing them in the electric furnace to a spongy mass, as a contact-material for the manufacture of  $\text{SO}_3$ .

Hölbling and Ditz (Ger. P. 142144) employ as contact-substance the mixture of the *oxalates* of cerium, lanthanum, didymium, etc., obtained in the manufacture of thorium compounds for illuminating purposes. The prevailing compound in that mixture is that of cerium, which passes over into cero- and ceri-sulphate. The yield of  $\text{SO}_3$  is all the better, the greater the proportion of cero-sulphate, and the less basic it is. It is best to treat the oxalate mixture, or the oxides obtained by igniting it with sulphuric acid, drive off the excess of the latter and heat for some time to  $300^\circ$  to  $600^\circ \text{C}$ ., which process yields nearly completely cero-sulphate in a porous shape. When this is used as contact-substance at the well-known favourable temperatures, pyrites-roasting gases yield a proportion of  $\text{SO}_3$  equal to that obtained with platinum, that is, nearly the

quantitative yield of  $\text{SO}_3$  from the  $\text{SO}_2$  contained in the gas, and quite as much with gases poor in  $\text{SO}_2$ . This mixture of the sulphates of the rare earths yields much better results than the pure sulphates of each of them. They may be employed by soaking asbestos, burnt clay, or other porous substances with a solution of those sulphates, and they retain their activity after a long use. If a deterioration of efficiency is observed, the masses are redissolved in sulphuric acid; the solution is filtered and evaporated, and the residue ignited at  $300^\circ$  to  $600^\circ$ .

According to Ger. P. 149677 of the same inventors the admixture of *neodidymium*, and especially of *praseodidymium*, sulphate has a very favourable influence on the catalytic action. With these contact-masses the purification of the roaster gases from arsenic is unnecessary, as this is retained in the mass.

Hallock (Amer. P. 930471) employs preparations of *radium* or *polonium* as contact-substances.

#### D. Absorbing-apparatus.

For the absorption of  $\text{SO}_3$  we must take into account the considerable quantities of water introduced into the process by the operations of washing and drying. These are converted into dilute acid, and must be brought up to  $\text{H}_2\text{SO}_4$  by means of  $\text{SO}_3$ . In the Ludwigshafen process the quantity of  $\text{SO}_3$  and  $\text{SO}_2$  taken out of the gases by the washing-operation is from 6 to 8 per cent. of the total. Much more is taken up by the operation of drying the gas. With gases of 7 vol. per cent.  $\text{SO}_2$  the weight of  $\text{SO}_3$  per cubic metre is 250 g. If the gases leave the washers at  $25^\circ\text{C}$ ., saturated with moisture, they will contain per cubic metre (at a tension of 23.5 mm.) 27.3 g.  $\text{H}_2\text{O}$ , corresponding to 121.3 g.  $\text{SO}_3$ , or nearly half of the above 250 g. Altogether about 60 per cent. of the  $\text{SO}_3$  formed is converted by water into  $\text{H}_2\text{SO}_4$ , leaving 40 per cent. at disposal in the free state.

Stone (Amer. P. 695180; *J. Soc. Chem. Ind.*, 1902, p. 476) describes an apparatus for cooling and absorbing sulphuric anhydride composed of a number of pipes and presenting no special interest.

Herreshoff (Amer. P. 722981 of 17th March 1903) passes into a vessel, provided with a cooling-jacket close to its bottom,

the vapours of  $\text{SO}_3$ , and at the same time, enough water or dilute acid to produce an acid of the desired strength.

Schlamp vom Hofe & Company (Ger. P. 166599) employ a tower, consisting of a number of compartments, all of which are divided by an inside plate in such manner that one side forms a cooling-chamber with stopped bottom and a cooling-coil entering at the top, and the other side an absorbing-chamber. There is always an absorbing-chamber above a cooling-chamber, and *vice versa*. The absorbing-acid passes first into the cooling-chamber and from this into the absorbing-chamber which contains a packing for the acid to run down on, and to meet the ascending vapours of  $\text{SO}_3$ . This is shown in Fig. 516.

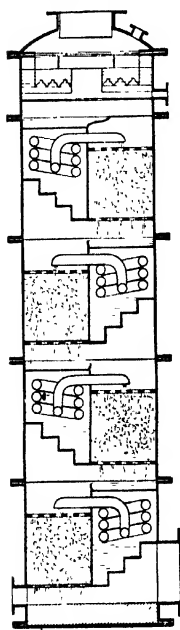


FIG. 516.

The Deutsche Ton and Steinzeug A. G., Berlin, recommend for absorbing  $\text{SO}_3$  the 'Cellarius receivers, shown in Fig. 517.

Cottrell (B. P. 21147 of 1907; Amer. Ps. 866843 and 866844; Fr. P. 382179; Ger. P. 208740) obtains the whole of the  $\text{SO}_3$  formed by the contact-substance in the form of sulphuric acid by suitably varying the humidity and temperature. The contact-gases are moderately cooled and passed through or

ever water or dilute sulphuric acid, or these liquids are injected in the form of spray to such an extent that the desired concentration is obtained.

Boult (B. P. 8528 of 1911) promotes the absorption of  $\text{SO}_3$  in sulphuric acid by reducing the temperature of the gas and of the absorbing-acid to a definite point, and by increasing the quantity of the absorbing-acid relatively to the quantity of  $\text{SO}_3$  in the gas to, or above a certain proportion (43:1). Thereby a fuming acid is stated to be obtained of a concentration that has not heretofore been possible. The Amer. P. of Irving J. Cox, 1002824, describes the same invention.

The process of I. J. Cox and the Du Pont de Nemours Powder Company (*suprà*, p. 1272) is specially intended for this case as well.

The amount of *acid gases escaping absorption* from contact-apparatus has been very carefully watched by the British Alkali Inspectors, *e.g.* in the *38th Report*, p. 16; in the *40th Report*, pp. 28, 121, 160, 179; and in the *41st Report* (for 1904), pp. 18, 92, 93, 132, 147, 151; the final result being that much progress had been made in this direction, but that full success had not yet been attained. The same observation is made in the *42nd Report* (for 1905), pp. 153 and 156.

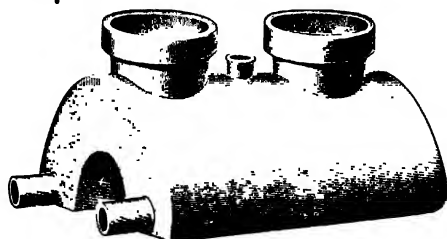


FIG. 517.

Ljungh (*Chem. Zeit.*, 1909, p. 143; *Chem. Centr.*, 1909, i. 1201) describes the testing of the waste gases from the catalytic manufacture of  $\text{SO}_3$  for the acid contained in them; his method presents nothing new.

#### E. Purification of Sulphuric Acid made by Catalytic Processes.

The sulphuric acid made by contact-processes, especially by the Grillo-Schröder process (*suprà*, pp. 1309 *et seq.*) is coloured dark by impurities, probably of organic nature. According to Max Liebig (Ger. P. 164722) it can be easily purified, in every state of concentration, by lead or barium peroxide, in the cold. Lead peroxide, *e.g.*, is added to it, with constant stirring, in slight excess, until it is no more dissolved, but forms a brown precipitate. The acid during this treatment gets heated, wherefore in the case of fuming acid the addition of  $\text{PbO}_2$  must take place gradually. The acid is then passed through a sand filter; it is as clear as water, does not darken later on and is free from impurities, especially  $\text{SO}_2$  and iron, except traces. Fuming acid does not become as clear as water, but takes a yellowish colour. Other oxidising agents, like nitric acid, permanganates, or hydrogen peroxide, do not act in the same way.

F. *Manufacture of SO<sub>3</sub> from By-products.*

*Acid-tar (sludge-acid)*, as obtained in the chemical treatment of petroleum, paraffin, and the like (*vide supra*, p. 1179), is utilised for the manufacture of SO<sub>3</sub> by J. D. Starck (B. P. 12028 of 29th August 1889) in the following manner:—The acid-tar is fed in at the lower end of an inclined iron retort, within which revolves an endless screw, for the purpose of drawing outwards the residual coke-like mass. The sulphur dioxide and water produced are freed from water and hydrocarbons by means of a condenser and wash-chamber; they are then dried in a sulphuric-acid tower, mixed with a suitable proportion of dry air or oxygen, and conducted through a tube containing platinised asbestos or other contact-substance. The SO<sub>3</sub> produced is condensed or absorbed in sulphuric acid, and the residual SO<sub>2</sub> is passed into ordinary vitriol-chambers.

*Recovery of sulphuric anhydride from waste materials containing such*, as obtained in the manufacture of coal-tar colours. —This is the object of a proposal of Schulze-Berge (Ger. P. 35620), who employs a partial vacuum for distilling SO<sub>3</sub> from such mixtures by means of a special apparatus. Already, on 8th August 1885, E. D. Kendall (Amer. P. 323583) prescribes the distillation in a partial vacuum for recovering the SO<sub>3</sub> from a mixture of fuming sulphuric acid with organic substances, in order to lower the temperature and to produce less SO<sub>2</sub>.

Gmehling (*Chem. Centr.*, 1906, i. p. 1060; *J. Soc. Chem. Ind.*, 1910, p. 376) describes the manufacture of SO<sub>3</sub> from the gases obtained in the extraction of copper from low-grade ores in Chile, by the Schröder-Grillo process (p. 1389). A yield of 90 to 96 per cent. of the theoretical amount of SO<sub>3</sub> is obtained, with a consumption of 0.75 kg. of fuel for 1 kg. S.

Carey, Heshop, and the United Alkali Company (B. P. 10317 of 5th June 1900) treat the *waste gases from the Claus-Chance process*, containing *sulphuretted hydrogen*, for the recovery of alkali-waste in the following manner:—The gases are passed with air through a furnace to burn the H<sub>2</sub>S into SO<sub>2</sub>, then dried in a tower by sulphuric acid, and then passed over or through a catalytic agent, such as platinised asbestos or iron oxide, maintained at a suitable temperature, to obtain SO<sub>3</sub>.

According to the *Alkali Inspectors' Reports*, No. 38, p. 15, this process was successful on the small scale, but was found too expensive to be introduced into actual practice. *Report* No. 41, p. 78, states that an experimental plant, erected in 1903, had been stopped after exhaustive trials. The results obtained were said to be satisfactory, but the cost of dealing with such large volumes of gases would probably be too great.

The United Alkali Company (Ger. P. 157589) passes  $\text{H}_2\text{S}$ , mixed with air, over finely divided platinum or other contact substances, thus producing the reaction:  $\text{H}_2\text{S} + 2\text{O}_2 = \text{H}_2\text{SO}_4$ . The contact-substance is spread on a stratum of sodium sulphate. This treatment has been found successful for the waste gases from the Claus-Chance process, containing about 1.5 per cent.  $\text{H}_2\text{S}$  and 1.5 per cent.  $\text{SO}_2$ , unmixed with air, which are passed through an iron apparatus, the first section of which is filled with broken bricks or the like and heated up to about  $540^\circ$  by outside fire, and the second section with the contact-mass. The first section causes the heating-up of the gases to about  $538^\circ$ , and a yield of 90 per cent. The waste heating-gases from the first section are passed round the second section, in order to keep the temperature of the contact-mass at the requisite height. (This process is evidently identical with that which has just been mentioned.)



## CHAPTER XII

### OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID

ALL the other processes which have been proposed for producing sulphuric acid, numerous as they are, can be dismissed with a very few words, since not one of them has had any technical success or promises to become successful in the future. The details can be found in the places quoted.

#### I. *Processes Dispensing with Nitre.*

Gossage (patent of 6th October 1857) burns sulphuretted hydrogen from soda-waste, cools the products of combustion, allows them to ascend in a coke-tower fed with water, runs the solution of sulphurous acid thus obtained down another coke-tower supplied with hot air, by which the  $\text{SO}_2$  is partly changed into  $\text{SO}_4\text{H}_2$ , and conveys the remaining  $\text{SO}_2$  into a lead chamber, where it is completely oxidised in the usual way. According to Gossage's own avowal (Hofmann, *Report by the Juries*, 1862, p. 9) this process is not practicable.

Petric (patent of 1st November 1852) allows a mixture of sulphur dioxide and water, heated to  $300^\circ$ , to meet a spray of water in pipes of earthenware or iron filled with silica or finely divided platinum, etc.

Houzé proposes (*Monit. Industr.*, vii. p. 65) to bring sulphur dioxide, air, and steam into contact in stoneware vessels at a temperature a little below red-heat. Similar vessels are said to permit distilling the acid by means of heated air or superheated steam without any bumping.

Surcouf. (Fr. P. 310660 of 7th May 1901) manufactures sulphuric acid from sulphur dioxide (and nitric oxide from ammonia) by means of ozone, heating the apparatus from the outside by steam or hot gases, in order to hasten the reaction.

Deacon showed in 1871 (*Chem. Trade J.*, 1889, vol. v.  
1442)

p. 193) that a mixture of  $\text{SO}_2$  and atmospheric air in the presence of a solution of cupric sulphate is converted into sulphuric acid, but this seems to have become very little known. Later on the same invention was made by Roessler, and was specially applied to the absorption of acid smoke; it has been described on pp. 528 *et seq.* It is hardly applicable to the manufacture of sulphuric acid proper, but possibly to that of copper sulphate from waste sulphur dioxide. The same process, extended also to salts of manganese, iron, or tin, has been patented by Clark (for Daguin), 3669 of 1888.

Schillot (Ger. P. 109484) passes  $\text{SO}_2$  and air through towers packed with pumice, and receiving steam and more air, at temperatures below the boiling-point of sulphuric acid, without any nitric acid.

Höhner (B. P. of 28th March 1854) employs chlorine in the presence of aqueous vapour for oxidising  $\text{SO}_2$ . The same process has been patented by Macfarlane (B. P. of 14th January 1863).

The Consortium für electrochemische Industrie at Nürnberg (Ger. P. 157043) produces at the same time sulphuric and hydrochloric acid by allowing a mixture of  $\text{SO}_2$  and chlorine to act upon water or aqueous hydrochloric acid in such quantities that on the one hand highly concentrated sulphuric acid, free from HCl, flows out, and on the other hand gaseous HCl escapes from the apparatus, according to the well-known reaction:  $\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{H}_2\text{SO}_4 + 2\text{HCl}$ . The hitherto difficult separation of hydrochloric and sulphuric acid is effected by employing a "reaction-tower," filled with cones, into which enter pyrites-burner gases and chlorine, and which is fed with only so much water as corresponds to the formation of gaseous HCl and sulphuric acid of 65 to 80 per cent. According to the Ger. P. 157044 of the same firm an excess of chlorine is employed, which secures the obtention of hydrochloric acid free from sulphuric acid, whilst, when working according to the first-mentioned patent, in the case of irregular currents of gas,  $\text{SO}_2$  and Cl may get into the condensers for HCl and there form  $\text{H}_2\text{SO}_4$ , which contaminates the hydrochloric acid. This is avoided by working with an excess of chlorine. (Their B. P. 14342 of 1902, taken out together with Askaniy and Mugdan, is for the same process.)

Bender (Ger. P. 195810) subjects a mixture of  $\text{SO}_2$  and O, with or without N, to the action of an oxy-hydrogen flame, *e.g.* by heating water in a furnace like a gas-producer up to the point of decomposition, burning sulphur at the same time and exposing the  $\text{SO}_2$  formed in the presence of an excess of oxygen or air to the action of the oxy-hydrogen flame. The latter furnishes both the heat necessary for the process, and the water required for the formation of  $\text{H}_2\text{SO}_4$ . The presence of nitrogen is useful for this process. In this way about 90 per cent. of the theoretically possible quantity of sulphuric acid is obtained (Fr. P. 377442; Amer. P. 900688).

Kühne (B. P. 17520 of 1908; Ger. P. 203541; Fr. P. 393461) exposes sulphurous fumes purified from flue-dust, and mixed with air and water or steam, to the action of a source of light, rich in ultra-violet rays, such as a mercury vapour lamp, enclosed in a quartz globe. The  $\text{SO}_2$  is thus almost completely converted into  $\text{H}_2\text{SO}_4$ , even when only 1 per cent. is present in the air. Aqueous solutions of  $\text{SO}_2$ , mixed with air, may be treated in the same manner.

Coehn and Becker (Ger. P. 217722) cause the combination of  $\text{SO}_2$  and O by exposing the mixture to ultra-violet light-rays at temperatures above  $300^\circ$ . The mercurial lamps employed for generating such rays must not be constructed on the lines most suitable for illuminating purposes, but they must work with low mercurial vapour pressures, which at higher temperatures allow of attaining a very rapid chemical action. (The application of ultra-violet light for oxidising  $\text{SO}_2$  is already mentioned in B. P. 10881 of 1904; it is at the present only of scientific interest.)

Hallock (Amer. P. 930471) subjects  $\text{SO}_2$  to the influence of an ionising agent, *e.g.* radio-active material in the presence of oxygen;  $\text{SO}_3$  is thereby produced.

*By Contact-processes.*—In Chapter XI., when treating of the contact-processes for the manufacture of fuming sulphuric acid or of  $\text{SO}_3$ , we have mentioned several inventions which at the same time aim at the production of hydrated sulphuric acid. There are also proposals for manufacturing this by contact-processes from the outset.

Thus Cottrell (Amer. Ps. 866843 and 866844) mixes the gases coming from the contact-mass with aqueous vapour in

such proportions that the whole of the  $\text{SO}_3$  is converted into a mist of  $\text{H}_2\text{SO}_4$ , which is thereupon separated from the gases by passing the mixture into a rotating shell within which are several concentric spaced cylinders forming "a series of functionally operative annular channels." A liquid seal guards the fitting of the non-rotating inlet and delivery pipes.

*By Electricity.*

Reynoso, in 1875, obtained a patent for causing electric sparks to pass through a compressed and cooled mixture of sulphurous acid and atmospheric air. The formation of  $\text{SO}_3$  from a mixture of 2 vol.  $\text{SO}_2$  and 1 vol. O by the electric spark was first observed in 1860 by H. Buff and A. W. Hofmann (*Ann. Chem. Pharm.*, cxiii. p. 129); Deville (*Bull. Soc. Chem.* [2], iii. p. 366) has observed that in the presence of strong sulphuric acid, which absorbs the  $\text{SO}_3$ , the whole gaseous mixture can be united to form  $\text{SO}_3$  in this way.

Wacker (Ger. Ps. appl. W10532 of 1894 and 10591 of 1895) proposes to prepare concentrated sulphuric acid by electrolysing water or dilute sulphuric acid through which a continuous stream of  $\text{SO}_2$  is being passed. He employs an earthenware vessel, divided into two cells by a porous earthenware diaphragm. Into the anode cell a slow stream of  $\text{SO}_2$  is introduced. In the cathode cell a magma of sulphur is formed, but little  $\text{H}_2\text{S}$  being given off. If hydrochloric acid is added, no sulphur is separated, the chlorine formed by electrolysis directly oxidising the  $\text{SO}_2$ . Other oxygen carriers may also be employed, such as sodium chloride or sodium sulphate, which acts by forming persulphuric acid; or else chlorates, nitrates, and so forth. [This process, in its present form, is a very peculiar one.] Cf. also Van Denberg's patent, p. 1452.

A. C. Johnson (Amer. P. 659236) sends a series of electric sparks into a chamber containing vaporous sulphuric acid gas [?] and introduces oxyhydrogen gas, which is exploded by the electric spark, whereby the acid-laden particles of moisture may be precipitated [?].

C. B. Jacobs (Amer. P. 704831 of 15th July 1902) forces  $\text{SO}_2$  through a porous anode, and oxidises it by the oxygen of water decomposed at the anode. The  $\text{SO}_2$  is oxidised in the lower

region of the bath, and the oxidation product is retained remote from the cathode. A sufficient current-density is maintained at the cathode to prevent the access of  $\text{SO}_2$  to it and to cause the rapid escape of hydrogen. The inventor claims (*Min. Ind.*, vol. x. p. 602) to attain an electrolytical efficiency of 54 per cent. with a potential difference of 2 volts and a current density of 15 to 20 amperes per square foot of anode surface.

A new process for the electrolytic preparation of sulphuric acid is described in A. Friedländer's Ger. P. 127985. Dilute sulphuric acid or water is electrolysed with application of diaphragms in such a manner that at the same time sulphur dioxide is passed into the anode cells, separated from the cathode cells in such a manner that the gaseous contents cannot communicate, keeping the contents under the requisite pressure, and conducting away the heat of reaction by internal or external cooling. In the cathode cells the reaction is  $\text{H}_2\text{SO}_4 = \text{H}_2 + \text{SO}_4$ . The hydrogen is conducted away; the  $\text{SO}_4$  ions migrate through the diaphragm to the anode, where they find  $\text{SO}_2$  and react with it thus:  $\text{SO}_4 + \text{SO}_2 = 2\text{SO}_3$ . The liquids remain perfectly clear, and there is no separation of sulphur, as in previous attempts at the electrolytic preparation of sulphuric acid from  $\text{SO}_2$ .

Boehringer and Söhne (Ger. P. 117129) attain the same object by adding to the sulphuric acid in the anode cell manganous sulphate, which serves as an oxygen carrier and thus converts  $\text{SO}_2$  into sulphuric acid, ultimately up to sp. gr. 1.78.

Kitsee (Amer. P. 869094) combines  $\text{SO}_2$  and O in the presence of moisture by "the action of an electric current, adapted to modify the chemical conditions of said gas to convert the same into sulphuric acid."

Johnson (Amer. P. 825057) saturates 20 per cent. sulphuric acid with  $\text{SO}_2$  and submits this solution to electrolysis, with application of lead electrodes; the cathode receives a copper covering. The result is sulphuric acid of 30 per cent. A portion of the acid is now withdrawn, the remainder is diluted, saturated with  $\text{SO}_2$ , and the electrolysis repeated.

Salom (Amer. P. 755247) oxidises  $\text{SO}_2$  in contact with water by electricity in a number of superposed vessels, each of which constitutes an electric cell.

Basset (B. P. 21475 of 1907; Fr. P. 370170) describes a cell

in which a solution of  $\text{SO}_2$  in dilute  $\text{H}_2\text{SO}_4$  is one electrolyte, and a solution of  $\text{N}_2\text{O}_4$  in dilute sulphuric acid the other electrolyte. The reaction is:  $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{NO}$ . The NO is oxidised into  $\text{NO}_2$  outside the cell.

Fischer and Delmarcel (*J. Soc. Chem. Ind.*, 1910, p. 694) describe experiments on the electrolytic oxidation of  $\text{SO}_2$  in aqueous solutions.

Briaille (B. P. 22434 of 1908; Fr. P. 393665; Amer. P. 928864) describes an apparatus for obtaining sulphuric acid from  $\text{SO}_2$ , at the same time concentrating and purifying it, by the electric current.

Garroway (B. P. 1755 of 1903) passes purified pyrites-burner gases into towers, together with air, previously ozonised by alternating-current electricity of high intensity and containing nitrogen oxides.

Riesenfeld (Ger. P. 229274) obtains an almost quantitative oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , by the action of electric sparks on roaster gases, or other mixtures containing  $\text{SO}_2$  and  $\text{O}_2$ , keeping the temperature during the whole process, or at least towards the end, below  $46^\circ$ . At such temperatures the reaction of ozone is not:  $\text{SO}_2 + \text{O}_3 = \text{SO}_3 + \text{O}_2$ , but  $3\text{SO}_2 + \text{O}_3 = 3\text{SO}_3$ . Air alone may be sent through an ozoniser and brought into action with  $\text{SO}_2$  below  $46^\circ$ .

*Ferrosilicium* in the granular state is employed as a contact-substance by A. von Grätzel (Ger. P. 157767), placed between the poles of a dynamo machine. By passing  $\text{SO}_2$  and water, eventually also air, through the apparatus, sulphuric acid is obtained without the intermediate formation of sulphur trioxide.

## II. Sulphuric acid from Sulphates.

The neutral sulphates of the alkalies, the alkaline earths, and lead are as good as unchangeable at a red-heat. The acid (primary) sulphates of the alkalies are first changed into pyrosulphates ( $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$ ); and the latter afterwards split up into neutral sulphates and sulphuric anhydride. This reaction, for obvious reasons, cannot be thought of for the manufacture of sulphuric acid proper, but only for that of fuming acid, under which head it has been noticed (cf. *suprà*, p. 1268).

Most of the other sulphates are no better adapted for the manufacture of sulphuric acid. Only those whose metallic radicals are but very slightly positive, more particularly ferric oxide and alumina, and the *acid* sulphates of other radicals, yield up their sulphuric acid at a comparatively low temperature, and consequently all or the greater part of it undecomposed; the other sulphates split up at a much higher temperature, mostly decomposing into metallic oxides, sulphur dioxide, and oxygen, yielding only a small portion of their sulphuric acid as such or as anhydride. Even if it were otherwise, their high price would make their employment for the manufacture of sulphuric acid impossible; most of them are themselves produced by means of ordinarily made sulphuric acid. From even the cheapest and most easily decomposable of all the sulphates in question, ferric sulphate, only fuming oil of vitriol can be made, and that only under especially favourable circumstances, as shown, p. 1265.

There only remain the sulphates occurring in some abundance in nature as such, viz., those of baryta, lime, and magnesia. The first of these has hardly ever been seriously taken up for this purpose; but the sulphates of lime (gypsum) and of magnesia (kieserite) have very frequently been the objects of inventions in this line (see below).

*Employment of Bisulphates (Nitre-cake, etc.).*—The Soc. Dior fils (Fr. P. 417816) makes sulphuric acid from alkaline sulphates or bisulphates, to which is added bauxite or aluminium sulphate, by heating in a muffle, so as to liberate  $\text{SO}_2$  and  $\text{SO}_3$ , which are then transformed into pure concentrated sulphuric acid. The aluminium sulphate, etc., is extracted from the residue with water and is treated with  $\text{CO}_2$ , to obtain an alkaline carbonate. An addition to this patent provides for the addition of coke-dust to the above-described mixture; this mixture is heated to  $1100^\circ$  to  $1250^\circ$  in a muffle furnace. When the mixture begins to lose its black colour and white specks appear, it is withdrawn from the furnace and treated as above.

Zahn (Fr. P. 389898; Amer. P. 921329) adds to sodium bisulphate just sufficient water to form hydrated sulphuric acid and the normal sulphate; say 6 or 7 kil. water to 100 bisulphate. Part of the sulphuric acid escapes on heating,

while the mixture becomes pasty, and in this state it is introduced into a muffle and calcined.

Prud'homme (Fr. P. 400030) obtains  $\text{SO}_3$ , or a mixture of  $\text{SO}_2$  and O, by heating natural or artificial sulphates in an electric furnace with simultaneous formation of anhydrous bases. By adding  $\text{SiO}_2$ , or  $\text{Al}_2\text{O}_3$ , or  $\text{Fe}_2\text{O}_3$  to the sulphates, the decomposition of the latter is rendered more complete.

Uebel (Ger. P. 226110) exposes bisulphate in a finely divided state to the action of superheated air, or steam, or fire gases, in a tower, the bottom of which consists of a calcining-hearth.

Benker (B. P. 1844 of 1907; Ger. Ps. 204354 and 204703; Amer. P. 899284; Fr. P. 381863) mixes nitre-cake with fine sand, or finely divided silicates, or anhydrous sulphates of Na, K, or Ca, in such proportions that the mass does not fuse on heating. Sulphuric acid may be distilled off and anhydrous  $\text{Na}_2\text{SO}_4$  remains behind, without the destruction of the apparatus which takes place when the bisulphate by itself is strongly heated. His Ger. P. 204703 gives the following instructions. One hundred parts neutral sodium sulphate and 25 parts nitre cake, both in the state of powder, are introduced into a heated muffle furnace, where the mixture at once gives off sulphuric acid without getting into the fused state. When the development of acid ceases, again 25 parts nitre-cake are added, but without any more neutral sodium sulphate, and this proceeding is continued, until altogether 100 parts nitre-cake have been put in upon 100 parts neutral sulphate. Now half of the charge is drawn out of the furnace, and the remaining half is spread out, so that more nitre-cake can be put in, and so forth, without ever having to put in any more neutral sulphate. The sulphuric acid vapours pass first through a cooler, where acid of  $55^\circ \text{Bé.}$  is condensed, amounting to about one-half of the total acid present. The vapours coming away from the cooler, consisting of  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ , and steam, are taken through a coke-filter, where by means of a little steam acid of  $40^\circ$  to  $50^\circ \text{Bé.}$  is condensed. If it were intended to produce anhydrous  $\text{SO}_3$ , a special condensing plant would have to be employed for the condensation of hydrated acid, and another such plant for condensing the  $\text{SO}_3$  in the last stage of the process.

*Sulphuric Acid from Calcium Sulphate.*—The enormous quantities of sulphuric acid occurring in nature in the shape of



gypsum or anhydrite, and nearly worthless in this form, have occasioned many proposals for their technical utilisation.

Tilghman (B. P. of 1st February 1847) passes steam over red-hot gypsum; CaO is said to remain behind, and SO<sub>2</sub>, O, and a little SO<sub>3</sub> to escape. For the identical process, Polony obtained an Austr. P. in 1887 (*Z. angew. Chem.*, 1888, p. 57).

Cary-Mantrand (Barreswil and Girard, *Dict. Chim. Ind.*, i. p. 37) exposes ignited gypsum to a current of dry HCl (whence does he get this?). CaCl<sub>2</sub> is formed; and SO<sub>2</sub>, O, and SO<sub>3</sub> escape. The same inventor decomposes a mixture of gypsum and coal at a red-heat by HCl gas, whereby CaCl<sub>2</sub>, CO, H<sub>2</sub>S, and S are formed.

O. Siemens (*Dingl. polyt. J.*, clxix. p. 207; Wagner's *Jahresber.*, 1863, p. 208) decomposes a fused mixture of gypsum and common salt by steam. There remains behind basic calcium sulphide with a little Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; the gases given off are SO<sub>2</sub>, HCl, and H<sub>2</sub>S; the latter is removed by conducting CO<sub>2</sub> and steam at the same time into the melted mass (?). This process is the subject of strongly adverse criticism by Buff (Wagner's *Jahresber.*, 1864, p. 170), who shows that the decomposition observed has been produced merely by the red-hot iron which forms the material of the apparatus.

Kuenzi (Wagner's *Jahresber.*, 1858, p. 95) fluxes gypsum with quartz, sand, clay, etc., to an easily fusible slag, whilst SO<sub>2</sub> and O escape. The same proposal was made by Frémy, and also by Archercau (*ibid.*, 1865, p. 271), by the latter for the purpose of utilising the oxygen as well.

O. Schott (*Dingl. polyt. J.*, ccxxi. p. 442) ignites sodium sulphate, gypsum, and coal in order to obtain a frit for glass-making; the SO<sub>2</sub> is to be conveyed into a lead chamber along with the other gas and converted into sulphuric acid.

Martin (*Bull. Soc. Chim.*, xxi. p. 47) prescribes making an artificial sulphide by smelting 1700 parts of gypsum, 1000 of ferric oxide, and 500 of coal in a blast-furnace; this is to be burnt like natural sulphides. In this case at most a monosulphide of iron will be obtained, and that will cost more than the best pyrites.

Scheurer-Kestner asserts that calcium or magnesium sulphate, when calcined with ferric oxide, preferably together with fluorspar, gives off sulphuric anhydride.

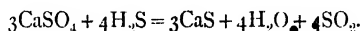
Basset (Fr. P. 331897) makes calcium sulphate, mixed with carbon and tar, into balls and heats these in a retort. The escaping gases are washed with water; the  $\text{CO}_2$  coming out is used for decomposing the  $\text{CaS}$  produced, and the  $\text{H}_2\text{S}$  thus set free is burnt, the  $\text{SO}_2$  formed being converted into sulphuric acid.

Cummings (Amer. P. 342785; B. P. by Lake, 7355 of 1886) calcines a mixture of gypsum and clay in a suitable kiln; a hydraulic cement is formed, whilst  $\text{SO}_3$ ,  $\text{SO}_2$ , and  $\text{O}$  are expelled, and are converted into sulphuric acid in the usual manner. [This is utterly hopeless with such dilute gases.]

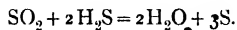
Köhsel (Wagner's *Jahresber.*, 1856, p. 57) decomposes gypsum, reduced by coal (that is,  $\text{CaS}$ ), by carbonic acid, burns the  $\text{H}_2\text{S}$  given off to  $\text{SO}_2$ , and conveys the latter into lead chambers.

The same proposal has been made several times later, in connection with special proposals for utilising the  $\text{H}_2\text{S}$ , of which only that of Chance (*suprà*, pp. 121 and 518) has been ~~found~~ to be practicable. At the present prices of pyrites even the Chance process does not seem to be economical in its application to gypsum.

Claus, Baranoff, and Hildt (Ger. P. 104188) treat a mixture of calcium sulphate and coal in retorts. The gases formed by the reaction  $\text{CaSO}_4 + \text{C} = \text{CaS} + 2\text{CO}_2$  contain up to 90 per cent.  $\text{CO}_2$  and less than 7.5 per cent.  $\text{CO}$ . They are made to act on  $\text{CaS}$  in the presence of water, so that  $\text{CaCO}_3$  and  $\text{H}_2\text{S}$  are formed. The  $\text{H}_2\text{S}$  is passed into retorts containing anhydrous  $\text{CaSO}_4$  at a red-heat. Here the reaction is:



This is always the initial reaction; but if an excess of  $\text{H}_2\text{S}$  is employed, this acts in the nascent state on  $\text{SO}_2$  and free sulphur is formed by Dumas's reaction:



Von Seckendorff (Wagner's *Jahresber.*, 1855, p. 54) decomposes gypsum by lead chloride at  $75^\circ$  into  $\text{CaCl}_2$  and  $\text{PbSO}_4$ . A mixture of the latter salt (5 mols.) with hydrochloric acid of  $33^\circ$  Tw. (4 mols.) at  $75^\circ$  C. almost entirely decomposes into  $\text{PbCl}_2$  (which is used for a new operation) and sulphuric acid

which is decanted and concentrated, the distilling HCl being condensed).

Shanks patented Seckendorff's process for England (9th October 1854).

Margueritte (patent of 22nd December 1854) decomposes lead phosphate by hydrochloric acid; hereby  $\text{PbCl}_2$  and phosphoric acid are formed; the latter, ignited with gypsum, yields calcium phosphate and sulphuric anhydride. The calcium phosphate and lead chloride, boiled together, regenerate lead phosphate, along with  $\text{CaCl}_2$ , which is worthless; so that the hydrochloric acid is always lost.

Bandiner (Wagner's *Jahresber.*, 1858, p. 102), Fleck (*Fabr. von chem. Prod. aus thier. Abfällen.*, p. 131), Reinsch (Wagner's *Jahresber.*, 1870, p. 167), and other authors mention the utilisation of the sulphuric acid of gypsum by treatment with a solution of ammonium carbonate, whereby ammonium sulphate is formed. This process has been used in France for some time, but it acts only incompletely.

Van Denberg (Amer. P. 642390) electrolyses calcium sulphate in a furnace in a molten condition in the presence of an excess of oxygen, thereby forming  $\text{SO}_3$ , and subsequently hydrating this.

Anzies (Fr. P. 420675) calcines a mixture of 408 gypsum with 148 ferric oxide at  $800^\circ$  to  $1500^\circ$ , and passes the mixture of  $\text{SO}_2$  and O thus obtained over oxides of manganese, tungsten, molybdenum or thorium at a temperature above  $200^\circ$ , in order to start the combination of  $\text{SO}_2$  and O.

Wedekind & Co. (Ger. P. 232784) roast a mixture of calcium sulphate, sand, and so much pyrites that the heat produced by the burning of the latter is sufficient for decomposing the  $\text{CaSO}_4$  by  $\text{SiO}_2$ . The B. P. is 20186 of 1910, and the Fr. P. 419871. The Amer. P. of F. Meyer and Wedekind & Co., 1008847, is for the same process.

Hilbert (Ger. P. 207761) makes  $\text{SO}_3$ , together with glass, by heating calcium sulphate with sand and alkaline sulphates.

Trey (*Z. angew. Chem.*, 1909, pp. 2375 to 2377) describes his laboratory experiments on the production of sulphuric acid from gypsum by heating with pure silica or sand, also with addition of 0.5 per cent. ferric oxide. In all cases the reaction took place pretty quickly and practically completely, but the

$\text{H}_2\text{SO}_4$  driven out was decomposed at the high temperature of the process into  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , so that the gases would have to be subjected to a catalytic process, in order to obtain  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$ .

### III. *Calcining Pyrites with Salt.*

Kenyon and Swindells (B. P. of 21st May 1872) calcine the chlorides of sodium or potassium with iron- or copper-pyrites, and treat the gas with nitric or chromic (!) acid in high towers, in order to convert the sulphurous into sulphuric acid; at the same time chlorine is given off. Wagner (*Jahresber.*, 1874, p. 272) points out that in this process the sulphuric acid must remain behind in the shape of alkaline sulphates.

## CHAPTER XIII

### BY-PRODUCTS OF THE MANUFACTURE OF SULPHURIC ACID

THE most important of these in the case of cupreous pyrites is the copper itself, together with the iron oxide (obtained in this case in a sufficiently pure form), sometimes also with silver; we shall treat this subject more in detail later on. From non-cupreous pyrites, however, iron and zinc are only exceptionally obtained. We do not, of course, refer to metals the production of which is the principal object of the whole process.

Besides, thallium and selenium may be mentioned as by-products of sulphuric-acid making.

#### I. *The Cinders from Non-cupreous Pyrites.*

We have described their composition, *suprà*, p. 446. They are frequently used as *ballast for making roads*; they yield very firm, dry, and even roads, which, however, are soon ground into dust by vehicular traffic, and in wet weather are then very muddy. Besides, the rain-water washes out iron and zinc sulphates, and may carry these into neighbouring wells (Sarrazin, *Arch. Pharm.*, ccix. p. 418).

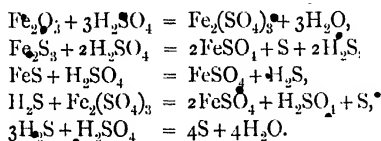
These cinders have frequently been proposed for the *absorption of sulphuretted hydrogen gas*, and really seem to have been here and there employed for purifying coal-gas and for disinfecting cesspools (*Z. für Chem. Gossgeu.*, i. p. 70). This, however, cannot be done extensively, as the cinders do not act anything like so energetically upon  $H_2S$  as precipitated ferric hydroxide or bog-iron ore, and therefore the purifying-apparatus would have to be made of enormous dimensions. Probably more success is obtained when using those cinders in the manufacture of ferrous sulphate for neutralising the sulphuric acid formed in the oxidation of bituminous lignite slates; formerly metallic iron used to be employed for this purpose.

It has also been proposed to utilise the pyrites-cinders or the "purple ore" (see below) for decomposing solutions of alkaline sulphides, but in this case the action is too imperfect. But after converting the ferric oxide into a "ferrite" by ignition with soda, the compound thus formed has an energetic action upon solutions of alkaline sulphides, upon which are founded the processes of Arrott and of Ellershausen (see Vol. III., 3rd ed., pp. 310, 311).

A. and P. Buisine (see Vol. II., 3rd ed., p. 423) employ moistened pyrites-cinders for absorbing hydrogen chloride from gases containing very little HCl. Or else they convert them into ferric sulphate (*Comptes rend.*, 1892, cxv. p. 51) by heating with sulphuric acid 60° Bc. not above 300° C. The resulting grey mass is hardly soluble in water, but becomes soluble by hydration at somewhat higher temperatures. The product can be employed as a very cheap ferric salt, or it can be converted into ferrous sulphate by digestion with iron. [This is indeed very easy, as I have convinced myself, ferrous sulphate is manufactured in this manner both more cheaply and more conveniently than by dissolving scrap-iron in sulphuric acid. The mass obtained by heating the cinders with Glover-tower acid is dissolved in hot water, the solution is digested with scrap-iron until the reduction to  $\text{FeSO}_4$  is complete, evaporated to 27° or 28° Bc. (measured at 90° C.), and allowed to crystallise, a number of strips of iron being suspended in the vat.]

Ferric chloride can be made by absorbing the gases from salt-cake furnaces in cylinders charged with pyrites-cinders, which takes place with evolution of heat.

Buisine (Ger. P. 73222) also describes a process for recovering from pyrites-cinders ferrous sulphate and free sulphur by the following reactions:—



The ultimate products of these reactions, apart from steam, are only ferrous sulphate and free sulphur, which are easily separated.

Arnois (Amer. P. 413428) seeks to convert burnt pyrites into useful *paint* by treating it at a dark red-heat in an ordinary atmosphere with a mixture of calcium carbonate and common salt in various proportions. [No doubt the treatment applied to the residue from the manufacture of Nordhausen acid (*suprà*, p. 1263) might be applied to pyrites-cinders as well; but only in the case of very pure ores, like the Aguas Teñidas, can products be obtained of sufficient purity for the above-named purpose.]

A considerable quantity of pyrites-cinders is used for manufacturing *iron-cement*.

Mills (Ger. P. 86589) proposes to reduce pyrites-cinders to "*iron protoxide*" for use as a black paint or in pharmacy. The cinders are sifted, ground, mixed with "amorphous" metallic iron (probably "spongy iron" is meant, *cf.* below), and heated to a red-heat in the absence of air. The quantity of metallic iron required depends upon the percentage of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  present in the cinders; the latter requires much higher temperatures for reduction. For pharmaceutical purposes the impure protoxide thus obtained is dissolved in dilute sulphuric acid, precipitated by caustic-soda solution and the dried precipitate reduced by iron. [There are several doubtful points in this proposal; in no case will real protoxide,  $\text{FeO}$ , be obtained as a final product.]

#### *Manufacture of Iron from Pyrites-cinders.*

The most important use of pyrites-cinders is for the manufacture of iron, either in blast-furnaces or in the manufacture of wrought-iron from pig-iron in puddling-furnaces, Siemens-Martin furnaces, etc.

• Formerly ordinary pyrites-cinders (from non-cupreous ores) could not be employed for making iron, because they contained at least 4 per cent., and usually more than this, of sulphur. One of the first attempts at utilising such cinders for the manufacture of iron was made at the Chauny works, which, in 1873, exhibited iron made from non-cupreous pyrites-cinders, desulphurised by repeated roasting in a Perret's kiln in thin layers. For this purpose the plates of this kiln were charged alternately with cinders and with fresh pyrites, the heat produced in the burning of the latter causing a supplementary roasting of the cinders (Hofmann's *Ber.*, 1875, i. p. 164).

Since that time very much progress has been made in treating the pyrites, both lumps and smalls, in such manner as to desulphurise it more completely; but this can only be done if the ore is pure, *i.e.* contains very little or no zinc and lead sulphides. Such pure ores can be burned in lumps down to 2.5 or even 2 per cent., and in the shape of dust even below 1 per cent. sulphur in the cinders, and in this case they can be smelted like ordinary (somewhat impure) iron-ores. In England, during 1902, the maximum percentage of sulphur allowed by the iron-works buying pyrites-cinders was 2 per cent., in Germany 1.5 per cent.

It has frequently been attempted to employ the cinders of small ore in larger quantities for smelting in a blast-furnace without stopping it up, by conglomerating them in different ways, but without much success. A British patent was taken out by J. Cahen for this purpose (10th June 1875). He moulds the cinders into suitable cakes with tar, peat, and limestone, and smelts these in a blast-furnace; the pig-iron is said to be very pure, the sulphur being absorbed by the lime, and the peat assisting in the formation of volatile phosphuretted hydrogen (?). J. L. Bell also moulds the small ore with lime into bricks, which harden by drying, and uses them in a blast-furnace. All such artificial conglomerates are soon crushed by the great pressure in the blast-furnace, and thus act like the loose powder.

Henzel (Ger. P. appl. H12573) mixes pyrites-cinders with from 5 to 40 per cent. ground clay and a little water, and charges the mixture (which may be previously moulded into bricks) by means of spades into a blast-furnace. The powdered ore is kept together by a superficial fusion of the aluminium silicate, but remains porous and permeable for the reducing gases. [One cannot understand how such a simple application of extremely old technical principles could form the subject of a patent.]

The Georg-Marien-Hüttenverein (Ger. P. 61061) heats bricks, moulded from pyrites-cinders, by a special fire to the sintering point.

Wüst (Ger. P. 82120) mixes pyrites-cinders with 7 per cent. silicate of soda, moulds the mixture by pressing, and exposes it at a moderate temperature to the action of carbonic acid, by which free silica and sodium carbonate are formed. The silica



acts as a cement, the sodium carbonate promotes the fusion of the slag, and prevents the sulphur contained in the cinders from passing into the pig-iron. [If the application of silicate of soda is not too expensive, its decomposition would be more easily and quickly obtained by the waste acid liquors formed at most works.]

The Duisburg Copper-works (Ger. P. appl. D6242) mix pyrites-cinders with ground furnace scale (magnetic oxide of iron) or similar slags, if necessary also with lime, mould the mixture into bricks and dry these. According to whether lime has been employed or not, from 5 to 20 per cent. of slags is required. The product is sufficiently firm for use in blast-furnaces; owing to the admixture of slag, it is also porous and accessible for the reducing gases.

Meves (Ger. P. 154584) makes bricks of pyrites-cinders by the assistance of peat-waste, etc., for use in blast-furnaces.

Cornette (Fr. P. 409001) describes the preparation of briquettes from pyrites-cinders for blast-furnaces.

In England, bricks of purple-ore are made without any cementing substance, merely by strong pressure, for use in Siemens-Martin furnaces (*Z. angew. Chem.*, 1894, p. 9).

Richters (*Dingl. polyt. J.*, cxcix. p. 292) investigated the application of pyrites-cinders in a coke blast-furnace by the analysis of all the products. With a charge of 38 calcined magnetic iron-ore,  $1\frac{1}{2}$  black band, 25.5 cinders (containing 4.35 per cent.  $\text{SO}_3$  and 1.53 S in other forms), and 35 limestone, under especially favourable circumstances, pig-iron with only 0.022 per cent. of sulphur was obtained; when, however, the temperature was lower, even with only 12 pyrites-cinders to 53.5 other iron-ore and 33.5 limestone, the pig-iron showed 0.049, 0.088, 0.096, 0.224 per cent. of sulphur. With a mixture of 19.2 pyrites-cinders, 46.5 other iron-ores, 30.1 limestone, and 4.2 potsherds, the sulphur in the pig-iron varied from 0.033 to 0.060 per cent.; by adding another 3.77 potsherds the sulphur was increased to 0.110 to 0.146 per cent. The pig-iron poorer in sulphur always contained a great deal of silicon, up to 3.485 per cent.

The cinders from roasting Schwelm pyrites are said to furnish an excellent material for Bessemer pig, as they contain very little phosphorus and copper, which are so injurious to

the quality of steel. F. Schmidt (*Berg- u. Hütten. Zeit.*, 1878, p. 68) states the composition of these cinders as follows:—

Ferric oxide	.	.	.	90.547	} = 65.0056 Fe.
Ferrous oxide	.	.	.	0.520	
Iron bisulphide	.	.	.	0.574	
Lead sulphide	.	.	.	0.142	
Copper sulphide	.	.	.	0.026	
Manganous oxide	.	.	.	0.463	
Alumina	.	.	.	1.448	
Lime	.	.	.	0.388	
Magnesia	.	.	.	0.220	
Sulphur trioxide	.	.	.	1.110	
Phosphorous pentoxide	.	.	.	0.035	
Silica	.	.	.	3.447	
Moisture	.	.	.	0.897	
				99.817	

Paur (Ger. P. 8730 of 22nd May 1879) proposes to treat the crushed pyrites-cinders with a solution of alkaline permanganate, by which sodium sulphate and  $Mn_2O_3$  are formed. The first is washed out, and the residue forms a manganiferous iron-ore, free from sulphur (but in all probability far too expensive).

The Elektrische Zinkwerke at Duisburg-Hochfeld (Ger. P. 173103); first desulphurise pyrites-cinders containing zinc, on the two hearths of a reverberatory furnace, with utilisation of the gases from the hearth next to the fire-bridge, charging them first on the remoter hearth where the sulphur is driven off, and then moving them on to the first hearth, where they are mixed with a reducing agent (carbon in some form). When the zinc has been driven off here, the heating is raised to the point of fusion, whereupon the mass is run out. Instead of moving the desulphurised cinders from the second on to the first hearth, they may be left in their place, and the way of firing may be changed in such manner that the second hearth receives the first fire-gases, and the first hearth the gases coming from the second.

The Internationale Wasserstoff A. G., Franklurt (Ger. P. 220889) employ pyrites-cinders, completely freed from sulphur and volatile metals by heating, for the preparation of hydrogen, as they are easy to reduce to metallic iron, owing to their porosity and their resistance to fusion.

According to *Chem. Zeit. Rep.*, 1911, p. 496, several Upper Italian factories have recovered pig-iron from pyrites for several years past by the electrical furnace of Carcano. A ton of iron costs 48s., and it contains 0.039 to 0.058 per cent. S, 0.063 to 0.075 per cent. P., and 2 to 4.5 per cent. Si.

*Recovery of Zinc from Pyrites-cinders.*

Pyrites containing zinc, such as the Westphalian ore from Meggen, cannot possibly be desulphurised in the burners so well as purer ore, owing to the great heat required for decomposing the zinc sulphate. The cinders from such ores contain both too much sulphur and too much zinc to be useful for the manufacture of iron without a special treatment for removing these impurities.

P. W. Hofmann (*Z. Verein. deutsch. Ingen.*, xviii. p. 521) proposed the following process for utilising the cinders from Westphalian pyrites, which sometimes contain 6 per cent. of zinc:—The cinders contain the zinc as sulphate, which is only decomposed at a much higher temperature than is attainable in a pyrites-burner. The zinc sulphate can be washed out by water at 40°; but it contains too much iron sulphate to be saleable. If, however, a solution of 1.25 sp. gr. be mixed with a proportion of NaCl equivalent to the sulphuric acid contained in it, and heated to 30° C., a liquor of 1.38 sp. gr. is obtained, from which, on cooling, such a quantity of Glauber's salt crystallises that this alone pays all expenses. The mother-liquor contains chloride of zinc with more or less common salt and the sulphates of iron, zinc, and sodium. If evaporated to 1.60 sp. gr., all foreign salts are separated, and a solution of zinc chloride, with mere traces of sulphates and of iron, remains behind, which can be employed directly for pickling railway-sleepers. The residue from lixiviating the sulphates is allowed to lie a few days in the air to dry; most of it then falls to powder. When this is passed through a sieve, the fine dust is found to be almost free from sulphur, the rougher particles containing nearly all the sulphur in the shape of FeS. The dust might be employed in a blast-furnace.

At the Aussig works formerly the crude zinc sulphate obtained in just the same way was formerly worked up by the addition of calcium chloride (waste lye from the recovery of

sulphur) into "pearl-hardening" and zinc chloride. Owing to the want of a sufficient market, this manufacture has been discontinued.

Creutz (*Chem. Ind.*, 1883, p. 258) remarks that Hofmann's process has not been much used, because the reactions are not so smooth as he represented. The sodium sulphate remaining in the zinc-chloride liquor is prejudicial to its employment for pickling timber. Nor were better results obtained by mixing the solutions of sodium chloride and zinc sulphate in the cold, as recommended by the Amer. P. 236051. The formation of double salts of zinc and sodium is the cause of this difficulty. It is therefore best to employ calcium chloride (*cf.* above) in the following manner:—The pyrites-cinders are exposed to the weather as long as possible to oxidise the iron and manganese compounds and the sulphurous acid. They are then lixiviated with cinders containing 3 per cent. zinc; a solution of zinc sulphate is obtained of sp. gr. 1.16, containing next to no iron and only traces of manganese and cobalt. This liquor is mixed with waste calcium-chloride liquor from the Weldon process, of sp. gr. 1.116, leaving a small excess of zinc sulphate. Calcium sulphate is precipitated and is filtered off. The clear liquor, of sp. gr. 1.075, is boiled down in an iron pan with top heat, and a little bleaching-powder is added to precipitate manganese and cobalt as peroxides. At a concentration of 1.5, the last traces of calcium sulphate are precipitated, and the clear liquor now contains only zinc chloride with a little zinc sulphate, no more than is contained in the liquor obtained by dissolving scrap-zinc in commercial hydrochloric acid. This process has the drawback of requiring fuel for boiling down the liquor, but it furnishes a liquor entirely fit for pickling wood. The expense of boiling down is saved when the crude solution of zinc chloride is treated for the preparation of zinc hydrate (for purifying soda-liquors from sulphides) by addition of lime, and filtering through a sand filter.

Egestorff's Salzwerke (Ger. P. 23712) purify pyrites-cinders from zinc by weathering, lixiviating, adding to the liquor calcium or barium carbonate, and treating it with a current of air. In this case the iron is quickly precipitated, and there is obtained on the one hand an iron-ore free from zinc, on the other hand zinc salt free from iron.

The Königshütte Berg- und Hüttenverwaltung (Ger. P. 28465) roast pyrites-cinders, containing zinc, with common salt, and lixiviate with weak hydrochloric acid. The liquor in case of need is freed from copper and is cooled down to such a temperature that sodium sulphate crystallises out. The zinc remains in the mother-liquor, and is recovered in the usual manner, probably chiefly in the shape of crystallised zinc sulphate.

Kosmann (*Fischer's Jahresber.*, 1886, p. 268) regards all the processes hitherto employed for the above purposes as of doubtful economical value.

Herberts (Ger. P. 38780) treats pyrites-cinders containing zinc in an iron boiler under pressure with steam; the sulphates of zinc and iron are dissolved, ferric oxide remains behind. Another patent of the same inventor (Ger. P. 41333) contains some improvements.

Riemann (Ger. P. 38072; *Fischer's Jahresber.*, 1887, p. 510) contends that only a third part of the zinc is dissolved in this manner. He therefore returns to the roasting with salt, but adds ferric sulphate, obtained by treating ground pyrites-cinders with hot sulphuric acid. A mixture is made of the cinders with 8 or 10 per cent. of crude ferric sulphate, and 15 or 18 per cent. of common salt, and is roasted for several hours in a reverberatory or muffle furnace, with access of air, at a temperature not exceeding 500° C. The product can be lixiviated with water alone, without adding any acid; the washed residue contains only 1 or 1.5 per cent. zinc, 0.3 or 0.6 sulphur, and 55 iron, and is therefore a useful iron-ore. The liquor contains any copper present in the ore, zinc chloride, and sodium sulphate. These salts cannot be separated, as asserted, by boiling down to sp. gr. 1.53, owing to the formation of double salts of zinc and sodium, but by concentrating the liquor, when at sp. gr. 1.32 to 1.36, in the cold by means of a vacuum. It is claimed that this process really permits of utilising the cinders from German pyrites, hitherto so troublesome.

*Electricity* has also been invoked for precipitating the zinc from the liquors obtained by the above-mentioned processes, but this does not seem to be economical.

Perino (Ger. P. 46748) makes an intimate mixture of the ore with ferric nitrate, and exposes this to gentle heat; about

50° nitrous fumes are evolved and zinc sulphate is formed, whilst the iron sulphide is less easily acted upon. The process is finished at about 150° or 200°. [This cannot pay, even when recovering as much as possible of the nitric acid from the fumes.]

From the zinc solution, obtained by roasting the cinders with salt and lixiviating, a valuable *paint* can be obtained by precipitating, with a solution of barium chloride, a mixture of barium sulphate and zinc sulphide. This mixture is called *lithopone* and is largely employed as a non-poisonous substitute for white lead. It was exhibited at Düsseldorf in 1902, by the Schalke Chemical Company, which prepares it from the cinders of Westphalian pyrites.

Kellner (B. P. 7028 of 1901) grinds pyrites-cinders, treats them with aqueous sulphurous acid in order to convert the zinc into bisulphate, oxidises this by air to sulphate, converts this into chloride by means of NaCl or KCl, and electrolyses the  $ZnCl_2$ .

Wikander (Ger. P. 158087 of 1903) passes through the cinders, at a temperature of about 550°, HCl gas or a mixture of this with air, thus converting the zinc into chloride which is recovered by lixiviation. In this way the cinders may be treated in the shape of lumps, without grinding, as gaseous HCl penetrates much better than aqueous hydrochloric acid; it also acts on the iron compounds much less than the liquid acid. The slight quantity of iron dissolved may be removed by addition of zinc oxide. Cinders containing 5 to 7 per cent. Zn have been advantageously worked in this manner, recovering 90 per cent. of the zinc present with an expenditure of 5 to 7 per cent. HCl. After this treatment the cinders, now nearly free from zinc and sulphur can be used in blast-furnaces.

Thwaites (B. P. 27515 of 1906) lixiviates the cinders and uses the liquid over and over again for the same purpose until sufficiently concentrated, oxidising by air if desirable, and taking out the copper by scrap-iron. From the solution of zinc thus obtained most of the sulphate of iron may be removed by crystallisation; the remainder of the iron may be precipitated by zinc oxide, or by caustic or carbonated alkali. The same inventor, B. Ps. 24847 and 27426 of 1907, first adds to the liquor, from which the copper may or may not have been

removed, zinc oxide or carbonate, or both, then oxidises by air or by a suitable oxidising compound, separates the precipitate formed, adds a suitable sulphide to precipitate Cu, Pb, As, Tb, and Cd, removes the precipitate and adds a soluble sulphide in proportion insufficient to precipitate the whole of the Zn as ZnS. As a final step, after removing the white ZnS, the rest of the ZnS and any Mn, Ni, and CO may be precipitated by a soluble sulphide. His Ger. P. 218870 provides for the recovery of cobalt from the liquid filtered from the zinc precipitate, by treating it with an oxidising agent.

Kaiser (Ger. P. 189313) drives out the zinc from pyrites-cinders in the metallic form in an electric furnace by suitable treatment with reducing gases, whilst the iron remains in the furnace in the metallic form.

Edelmann (Ger. P. appl. E11865) removes the zinc from the cinders by sulphatising roasting in kilns, filled with roof-shaped packing, over which the finely ground cinders run down,  $\text{SO}_2$  being passed in at the bottom, and the necessary heat being produced by heating-tubes in the lower part of the kiln.

Siemens and Halske (Ger. P. 233252) add common salt to the cinders, remove the sodium sulphate by freezing out of the solution, precipitate the Zn by means of calcium carbonate, collect the  $\text{ZnCO}_3$ , convert this into sulphate by addition of sulphuric acid and obtain from this the zinc by electrolysis.

The Metals Extraction Corporation, Limited (Ger. P. 224922), extracts the zinc from pyrites-cinders, etc., by an aqueous solution of  $\text{SO}_2$ , saturated at least under the pressure of 1 atm.

#### *Recovery of Thallium and Selenium.*

In the flue-dust and the chamber-deposit of many descriptions of pyrites the rare metals *selenium* and *thallium* have been found. The former has hitherto no industrial application, apart from the employment of crystalline selenium in photometry, as its electrical conductivity changes in proportion to the intensity of the light that falls upon it.

*Thallium*, however, is manufactured on a comparatively large scale at Aussig and Mannheim; and it might possibly be found useful for optical glass, replacing the alkali: owing to its very high atomic weight (204) it gives, together with red-lead

and quartz, the specifically heaviest and consequently the most refractive glass hitherto known (Lamy).

The preparation of thallium from the flue-dust of Westphalian pyrites has been described by Schaffner (Wagner's *Jahresber.*, 1871, p. 1). The flue-dust was collected in a large brick chamber without being exposed to the action of nitrous vapours, the chambers being fed directly with nitric acid. It is coloured by ferric oxide, contains much arsenious acid, ferric sulphate, some zinc oxide, lead oxide, traces of antimony and silver, thallium sulphate, etc. Carstanjen (Wagner's *Jahresber.*, 1868, p. 10) found in it 3.5 per cent. thallium. On the sides of the chamber crystals were found of the compound  $As_2O_3$  and  $SO_3$ , discovered by Reich. The flue-dust is lixiviated by boiling with steam, with the addition of a little sulphuric acid, as a portion of the thallium seems to be present as basic sulphate, which would escape solution. After settling, the clear portion is siphoned off and filtered through calico; the residue is boiled again. From the liquid the thallium is precipitated as protochloride. The very impure reddish precipitate is washed with cold water and converted into sulphate by hot concentrated sulphuric acid, the heating being continued till all excess of acid is driven off. The sulphate is dissolved in water, filtered, and again precipitated by hydrochloric acid, the  $TlCl$  now being separated almost in the pure state. If it is not yet pure, especially if it contains arsenic, the operation must be again repeated. In order to remove all arsenic, sulphuretted hydrogen is conducted into the solution of thallium sulphate, which precipitates all the arsenic together with small quantities of thallium; the latter is precipitated from the filtrate by hydrochloric acid as perfectly pure  $TlCl$ , and converted into sulphate as above. The sulphate is reduced to metallic thallium by digesting its solution in a porcelain or stoneware dish with metallic zinc. The spongy metal obtained is washed with distilled water, pressed between blotting-paper, and melted in an iron or porcelain crucible, hydrogen or coal-gas being conducted through to prevent any oxidation; the heat should not be too strong, because it might volatilise the thallium. The melted metal, similar to mercury, is cast into small rods in paper moulds. It should be kept in boiled water, free from air, the vessel being closed whilst the water is boiling; but even



then the latter after a short time shows an alkaline reaction. It is best kept in a solution of zinc sulphate. It can also be obtained well crystallised by Woehler's process, viz., by suspending in the thallium solution a beaker with its bottom cut off, and its lower part closed with a bladder tied round; this is filled with water up to the level of the solution outside; a zinc plate is suspended in the water, and the latter connected with a platinum wire, which dips into the thallium solution and is bent into a spiral below the bladder.

Krause (*Dingl. polyt. J.*, ccxvii. p. 323) observes that the treatment of thallium protochloride with concentrated sulphuric acid is very unpleasant work in large quantities. He has found that the decomposition can be quickly and completely effected by a weak solution of Glauber's salt, say  $4^{\circ}$  to  $7^{\circ}$  Tw. He lixiviates the fine dust in a cask with water and steam, siphons off the settled liquid into a second cask, and adds to this solution of thallium sulphate hydrochloric acid; the  $\text{TlCl}$  subsides very quickly, if the liquid is well agitated, for instance by a current of air. After a short rest the clear liquid is run off, the cask is filled up with pure water, heated by steam, and crystallised sodium sulphate added till the solution shows  $7^{\circ}$  Tw. After strong agitation the decomposition is complete, and the liquid is siphoned off into a third cask, which is placed somewhat lower; here it is acidulated with sulphuric acid and the thallium precipitated by zinc. Like Schaffner, he washes the sponge with water free from air, presses and melts it. This process permits working continuously and without contact with fire.

Nietzki has made very detailed communications on thallium (Wagner's *Jahresber.*, 1876, p. 4). He found in the flue-dust of the Duisburg chemical works, where Westphalian pyrites is used, 0.1 to 0.2, sometimes even 1 per cent. thallium. The precipitation as  $\text{TlCl}$  is incomplete: it is true that  $\text{TlCl}$ , which is soluble in 500 parts of water, is much less so in the large excess of hydrochloric acid actually employed; but there remains even then 10 per cent. of the thallium present in the mother-liquor. Much more complete is the precipitation of thallium by potassium iodide as  $\text{TlI}$ , even from very dilute solutions of flue-dust. Therefore both the mother-liquors from the  $\text{TlCl}$  precipitate and the dilute extractions of flue-dust are

afterwards treated with KI. By boiling the TII with sodium sulphide the iodine is recovered as NaI; and the insoluble  $Tl_2S$  is worked up for  $Tl_2SO_4$  along with the  $TlCl$ . From the sulphate the thallium is obtained by electrolysis, to avoid its contamination with zinc. In this case crude thallium sulphate can be employed; whilst direct reduction with zinc is troublesome, owing to the evolution of arseniuretted hydrogen and the reduction of ferric salts, the ferrous sulphate soon forming a crust over the zinc and making it inactive. Nietzki even employs KI for volumetrically estimating thallium; but the solutions must not be too dilute.

Stolba's process (Wagner's *Jahresber.*, 1874, p. 1), allowing a thallium-alum or thallium-iron alum to crystallise from concentrated solutions of flue-dust, is only adapted for substances extraordinarily rich in thallium.

Woehler (*Ann. Chem. Pharm.*, clxiv., p. 74) states that thallium is more simply produced by fluxing the chloride with sodium carbonate and carbon. Twenty parts  $TlCl$ , 8 parts of dry  $NaCO_3$ , and 1 part of lampblack are mixed together and fluxed in a fireclay crucible at a moderate red-heat. A small loss occurs by some chloride volatilising; this can be avoided by stirring up the mixture with water, drying, and then fluxing.

Selenium was discovered (in 1817) by Berzelius in the chamber-deposit of the sulphuric-acid works at Gripsholm, at which Fahlun sulphur (obtained in roasting ores) was used. It also occurs in volcanic sulphur, e.g. 0.264 per cent. in the solfataras of Naples, according to Plipson (*Chem. News*, v. p. 337)—principally, however, in many descriptions of pyrites, so that the chamber-deposit of the Mansfeld and Oker work is the best source of it. Selenium occurs in several allotropic modifications, in regard to which we must refer our readers to the chemical treatises. Its specific gravity is given as 4.26 to 4.8, melting-point  $400^\circ$ , boiling-point about  $700^\circ$ . Selenium always occurs in very small quantities; but its characteristic reactions cause it to be easily discovered, and it becomes very much concentrated in the deposit of flue-dust. Some Har works' deposit is said to contain 10 per cent., that of the Eisleben works 9 per cent. of selenium; annually several cw are obtained in this way (Böttger and Kemper, Wagner's *Jahresber.*, 1860, p. 169). On selenium in French sulphuri

acids communications have been made by Kuhlmann, Personne, and Scheurer-Kestner (*ibid.*, 1872, p. 246)<sup>1</sup>; cf. also Lunge (*Chem. Ind.*, 1883, p. 128) and Davis (*J. Soc. Chem. Ind.*, 1883, p. 158).

The deposit contains free selenium, as the selenious acid formed by burning is reduced by sulphurous acid. Otto (*Lehrbuch d. Chem.*, 4th ed., i. p. 633) digests the deposit, previously washed with water, with aqua regia to oxidise the selenium, adds sulphuric acid, evaporates to dryness, driving off the other acids, treats the residue with water, and from the solution, by cautious addition of ammonium sulphite, first precipitates white mercurial chloro-seleniate, then from the filtrate, by more ammonium sulphite and sulphuric acid, the selenium itself. From the mercurial precipitate the selenium can be obtained by oxidising with nitric acid, evaporating, neutralising with sodium carbonate, fluxing with potassium nitrate, boiling with hydrochloric acid in order to reduce  $\text{SeO}_3$  to  $\text{SeO}_2$ , and precipitating the selenium from the solution by  $\text{SO}_2$ .

Liebe (Wagner's *Jahresber.*, 1860, p. 178) extracts the oxidised mass, after evaporation with sulphuric acid, with water, neutralises with soda-ash, evaporates to dryness, mixes the residue with an equal weight of sal-ammoniac, calcines the mass in a porcelain dish (when the sal-ammoniac reduces the  $\text{SeO}_3$ ), and washes with water, pure selenium remaining behind.

Böttger (*Dingl. polyt. J.*, clxxvi. p. 405) extracts the selenium from the chamber-deposit washed with water by means of a concentrated solution of neutral sodium sulphite, and filters it into dilute hydrochloric acid, which at once precipitates the selenium.

Nilsén (*Ber.*, vii. p. 1719) describes the working-up of the Fahlun chamber-deposit for selenium. This cannot well be done by Otto's process: it is better to employ potassium cyanide, 2 parts of which yield 1 part of selenium. The washed deposit needs only to be digested with a concentrated solution of potassium cyanide at 80° to 100° C. till its red colour has just been turned into pure grey; the residue is washed with boiling water, filtered, and hydrochloric acid added to the solution; selenium, at once precipitates in cherry-red flakes, as the liberated selenocyanic acid is almost instantaneously

decomposed into selenium and hydrocyanic acid; the sulphur dissolved at the same time remains in solution as sulphocyanic acid. The selenium thus obtained contains only a little copper, iron, and perhaps traces of mercury; it is obtained quite pure by dissolving in nitric acid, evaporating to dryness in a water-bath, subliming the anhydride in a current of dry air, and treating its solution with sulphurous and hydrochloric acids.

Kienlen (*Bull. Soc. Chem.* [2], xxiv. p. 440) showed that the selenium, being reduced by  $\text{SO}_2$  in the Glover tower, is dissolved in the sulphuric acid, to which it sometimes imparts a blood-red colour. When diluting the acid with three times its bulk of water, the selenium is precipitated. Glover acid contains up to 17.3 mg., chamber-acid 22.3 mg. per kilogram. If such sulphuric acid is employed for the manufacture of hydrochloric acid, the selenium is volatilised together with  $\text{HCl}$  and is deposited in the first receivers as a reddish mud containing 41 to 45 per cent.  $\text{Se}$ , whilst the hydrochloric acid holds up to 21.4 mg.  $\text{Se}$  per kilogram. The selenium is extracted from the mud by chlorine, which forms selenious and selenic acid. When the red colour has been destroyed the mass is filtered, the filtrate is boiled with hydrochloric acid, and the selenium precipitated by sodium sulphite.

Bornträger (*Dingl. polyt. J.*, ccxlvii. p. 505) found in the red mud from Glover-tower acid (made from Rio-Tinto pyrites), after washing and drying, 12.60 per cent.  $\text{Se}$  (with 76.30  $\text{PbSO}_4$ , etc.). He obtains the selenium from it by heating it in fireclay retorts at a red-heat, with exclusion of air, as a black metallic sublimate, which is freed from  $\text{As}_2\text{O}_3$  and  $\text{S}_2\text{O}_2$  by washing with strong caustic soda.

Divers and Shimosé (*Chem. News*, No. 1256) found in sulphuric acid made from Japanese brimstone 0.37 g. tellurium and 0.15 g. selenium per litre, and in the sediment from the same acid 10.5 per cent. selenium and 1.2 per cent. tellurium. Shimosé (*ibid.*, No. 1260) further describes the process employed by him for separating selenium and tellurium, viz., neutralising the sediment with sodium carbonate, removing the selenium by digesting with concentrated solution of potassium cyanide at a gentle heat (at first cold), diluting the mixture with water, and heating nearly to boiling. The solution, containing the selenium, is treated with hydrochloric acid in order to separate

the Se; on the other hand, the sediment from which the cyanide solution has been decanted yields tellurium by a treatment with sulphuric acid and a little nitric acid, and passing  $H_2S$  through the solution obtained.

Koch (Ger. P. 167457) recovers selenium from the flue-dust of the lead chambers by treating it with sulphuric acid of moderate concentration ( $50^\circ$  B $\acute{e}$ .) and potassium permanganate at  $50^\circ$  to  $60^\circ$ , adding NaCl, diluting the liquid, filtering and precipitating from the filtrate the selenium by reducing-agents.

The process described by Littmann (originating from L. Deutsch), by which selenium is recovered from the sludge of Glover-towers, has been described *suprà*, pp. 1070 *et seq.*

Threlfall (*Roy. Soc. Proc.*, lxxix., A. p. 167; *Chem. Centr.*, 1907, ii. p. 124) purifies selenium by dissolving in nitric acid, boiling off the excess of the latter, subliming the  $SeO_2$ , dissolving it in water and filtering, precipitating free Se by reduction with HCl and  $SO_2$ , washing with water, again converting into  $SeO_2$  and subliming this in a current of air in order to remove any traces of tellurium. Selenium after this treatment shows absolutely no Hg, only 0.00038 per cent. As, or less than 0.01 per cent.  $SeO_2$ .

## II. The Extraction of Copper from Pyrites-cinders.

This manufacture cannot properly be regarded as a by-work done in sulphuric-acid making; with as much, if not with greater, right the latter might be considered a secondary branch of the extraction of copper, since in the cupreous ores the value of the copper mostly exceeds that of the sulphur contained in them; but if the value of the final products be counted, that of the sulphuric acid certainly mostly far outweighs that of the copper. Even in the large English works nowadays the extraction of copper from the cinders is rarely carried out in the chemical factory itself; the former operation is concentrated in a few works erected in the centres of the chemical trade, which receive the burnt ore from a whole group of chemical works. One of the largest pyrites-mining companies, the Tharsis Sulphur- and Copper-extracting Company, supplies its ores to the consumers only on condition of returning the burnt ore to the copper-works belonging to the same company.

A similar establishment was founded at Duisburg by a number of Rhenish manufacturers, likewise based on the extraction of Spanish pyrites-cinders. Although the production of copper thus does not belong to the usual cycle of vitriol- and alkali-works, yet it is most intimately connected with it, especially in Great Britain; and a description of that production does not seem out of place here.

The percentage of copper in the ores in question (*cf.* p. 79) is mostly so small, rarely above 4 per cent., that its extraction by smelting would not pay. This can only be made possible at the outset by carrying on the first necessary operation (the calcining or burning) in such a way that the calcining-gas does not go away into the air, but is taken into lead chambers and sulphuric acid made of it, which helps to pay for the ore. But something else is necessary in practice. The cinders from burning the ore are still too poor in copper to be smelted in the usual way. They might possibly be smelted for "coarse metal," with a mixture of a little green pyrites, silicious sand, and slags; and this coarse metal might be sent to copper-works for further treatment; but in that case only a portion of the copper would be obtained, and the expense would be barely covered. When the quantity of poor ore coming into the market became larger, this way of utilising it was out of the question. Other drawbacks in smelting for coarse metal, as they were observed at Oker, will be mentioned below.

Accordingly, since 1865, the copper of poor ores is always extracted *in the wet way*. From time immemorial the pit-waters arising from weathered ore have been precipitated by metallic iron, and *cement-copper* obtained in this way; but the processes for converting the copper purposely into such compounds that it becomes capable of being dissolved and precipitated, all date from a recent period. Exact descriptions of the former processes are found in Percy's *Metallurgy*, more recent processes in Stölzel's *Metallurgie*, i. p. 714, and in Hofmann's *Ber.* of 1873, p. 885 (this article is from the pen of Professor Kerl). Most of the volumes of Wagner's *Jahresber.* contain the literature of this branch.

It is beyond the scope of this book to enter specially upon all the proposed or really carried-out processes for copper-extraction in the wet way; we must refer the reader to the

authorities just mentioned, and we shall only describe in detail that process which for a number of years has been exclusively employed for working up the cinders from sulphuric-acid works, viz., the *roasting with salt*, followed by the *precipitation by means of iron*. It appears that the interesting process of lixiviating by means of ferrous chloride, originally proposed by Schaffner, but best known in the shape given to it by Sterry Hunt and Douglas, is not in use at vitriol-works or at the copper-works in immediate connection with these; we must therefore, in respect of this also, refer to the originals.

The first attempts in this way seem to be referable to Hunt (B. P. 8356 of 21st January 1840), and especially to Longmaid (B. Ps. 9496 of 20th October 1842, and 10004 of 1844). The latter exactly described the principles of the process, as it is carried out to the present day, certainly with a view to making salt-cake and chlorine as the chief products; and he also worked it out on a large scale; so that he must be regarded as the founder of the wet extraction of copper. Certain small improvements were patented at different times—for instance, by Gossage B. P. 13177 of 17th July 1850. We find much later, in 1856, the process started with a good deal of noise as a novel one, by Bechi, of Florence, and Haupt, of Freiberg, for working the ores at Capanne Vecchie (Wagner's *Jahresber.*, 1858, p. 68). It is strange that, sixteen years after Longmaid, such a distinguished metallurgist as Gruner should ascribe the success of Bechi's process less to the influence of the common salt than to the fine grinding. Bechi and Haupt's process was patented in England in the name of Hähner, as B. P. 571 of 7th March 1856; it differs from Longmaid's process merely by much greater complication, such as calcining three times instead of once, and has long since been given up. Schaffner (Wagner's *Jahresber.*, 1862, p. 119; 1871, p. 139) improved the process in several respects; but it was carried out on a large scale chiefly in England, by Phillips, Henderson, Tennant, and others.

Spongy iron was first employed by Gossage; it was again patented by Aas in 1861, and by G. Bischof in 1862 (Wagner's *Jahresber.*, 1862 p. 133, and 1863, p. 153).

The process now generally employed in England has been

principally described by Clapham (*Chem. News*, xxiii. p. 26), Wedding and Ulrich (Wagner's *Jahresber.*, 1872, p. 152), Gibb (*Chem. News*, xxxi. p. 156, and several publications of the Tyne Chemical Society), by myself (*Dingl. polyt. J.*, cciv. p. 288; ccxiv. p. 466; ccxv. pp. 54 and 229; ccxix. p. 323); the process at Oker by Bräuning (*Preuss. Z. f. Berg-, Hütten- u. Salinenwesen*, 1877, p. 156). Several more recent descriptions, e.g. that by Egleston (*Fischer's Jahresber.*, 1886, p. 170), contain nothing of any importance. A paper by Bode (*Dingl. polyt. J.*, ccxxxii. pp. 254, 357, and 428) gives a very complete survey of all the previous ones. The notes of E. A. Mebus, published by Jurisch, are also of interest, especially concerning the recovery of silver (*Chem. Ind.*, 1894, p. 378). The process and plant used at Natrona, near Pittsburg, are described by Clemmer, *Min. Ind.*, vii. p. 197, and ix. p. 283. Kothny (*Metallurgie*, 1911, viii. pp. 389 to 399) describes his investigations on the chemical processes going on in the roasting of burnt pyrites with salt. In the following description the above sources are used, as well as notes taken by me at several copper-works.

The three most important ores employed in the English sulphuric-acid factories contain from 47 to 49 per cent. of sulphur, and the following quantities of copper and silver:—

	Copper.	Silver.
	Per cent.	Ounces (troy) per ton.
Rio-Tinto . . .	3.80	1.20
Tharsis . . .	3.50	0.75
San-Domingo . .	3.70	0.75

(N.B.—An ounce troy is = 480 gr.; there are 32,666 oz. troy to the ton.)

The "ordinary copper-ores" at Oker generally consist of 50 per cent. iron-pyrites, 23 per cent. copper-pyrites, 6 blende, 2 galena, 9 gangue (complete analyses, p. 66).

The percentage of sulphur in the cinders as they are supplied by the acid-works varies extremely; hardly ever falling below 2 per cent., it sometimes rises above 10 per cent.



The latter, however, results from very bad work indeed; but 4 to 5 per cent. is considered very fair work; and as much is indeed required for the wet copper-extraction. The sulphur may even amount to one and a half times as much as the copper, but no more. At Oker the cinders are delivered to the extracting-works with 5 to 8 per cent. sulphur and 6 to 9 per cent. copper. If the pyrites arrives too thoroughly burnt from the acid-works, the copper-works add a little green pyrites in order to have sufficient sulphur for the first stage of their process.

The following analyses by Gibb show the composition of the pyrites-cinders as the copper-works receive them:—

	Rio-Tinto.	Tharsis.	San-Domingo.	Ytterøyen. (Norway.)
Copper* . . . .	1.65	1.50	1.55	1.01
Iron* . . . .	3.64	3.23	3.76	3.33
Sulphur* . . . .	3.53	3.15	3.62	3.10
* Cupric oxide . . . .	2.75	2.56	2.70	0.39
Zinc oxide . . . .	2.02	0.55	0.47	6.46
Lead oxide . . . .	0.47	0.70	0.84	0.06
Silver . . . .	0.0037	0.0023	0.0023	...
Cobaltic oxide . . . .	0.007	0.032	0.033	...
Bismuth oxide . . . .	0.013	0.010	0.013	...
Calcium oxide . . . .	0.20	0.25	0.28	2.30
Ferric oxide . . . .	77.40	77.00	78.15	68.06
Sulphuric acid . . . .	6.10	5.25	5.80	6.56
Arsenic acid . . . .	0.24	0.17	0.25	0.05
Insoluble residue . . . .	1.45	5.85	1.85	8.74
Total . . . .	99.46	100.25	99.31	100.06

\* Calculated as  $\text{Cu}_2\text{S}$  and  $\text{Fe}_2\text{S}_3$ .

Phillips states the following as the composition of cinders from San-Domingo bre:—

Sulphur . . . .	3.66
Arsenic . . . .	0.25
Iron . . . .	58.25 = $83.0 \text{ Fe}_2\text{O}_3$
Copper . . . .	4.14
Zinc . . . .	0.37
Cobalt . . . .	trace
Lead . . . .	1.24
Lime . . . .	0.25
Insoluble . . . .	1.06
Moisture . . . .	3.85
Oxygen and loss . . . .	26.93

Wedding and Ulrich found in samples from Widnes (a) and Hebburn (b):—

	Sulphur.		Copper.	
	a.	b.	a.	b.
Altogether . . . .	4.12	3.75	4.08	5.75
Of this soluble in water . .	Per cent. 43.0	Per cent. 37.0	Per cent. 46.0	Per cent. 26.1
"          HCl . . . .	55.0	59.0	22.2	13.3
In the residuc . . . .	2.0	4.0	31.8	60.6
	100.0	100.0	100.0	100.0

According to Hjelt the cinders from Spanish pyrites contain 0.19 per cent. arsenic.

The Oker cinders showed, on an average of a month's work:—

	Per cent.		Per cent.
Copper (principally as CuO) . .	7.83	Sulphur . . . . .	3.80
Iron (principally as Fe <sub>2</sub> O <sub>3</sub> ) . .	40.53	Sulphuric acid (corresponding to 3.8 S) . . . . .	9.51
Lead (as PbO) . . . . .	2.09	Alumina . . . . .	4.43
Silver . . . . .	0.008	Other gangue . . . . .	11.65
Zinc (as ZnO) . . . . .	1.95		
Manganese (as Mn <sub>2</sub> O <sub>4</sub> ) . . . .	0.40		

The sulphur must be mostly in combination with iron, since unburnt crude ore could be seen as cores on breaking up the lumps. The sulphuric acid is partly combined with lime, partly with metals, probably, as may be inferred from the well-known processes of roasting, in the first line with CuO and ZnO, in the second line with FeO or Fe<sub>2</sub>O<sub>3</sub>. From this the following would appear to be the most probable composition of the cinders:—

	Per cent.
CuO . . . . .	9.80
Fe <sub>2</sub> O <sub>3</sub> . . . . .	53.14 = 37.2 Fe
FeS <sub>2</sub> . . . . .	7.13 = 3.8 S
PbO . . . . .	2.25
Ag . . . . .	0.008
ZnO . . . . .	2.43
Mn <sub>2</sub> O <sub>4</sub> . . . . .	0.57
SO <sub>3</sub> . . . . .	9.51
Al <sub>2</sub> O <sub>3</sub> . . . . .	4.43
Other gangue . . . . .	11.65
	<hr/> 100.918

These cinders were formerly utilised in small blast-furnaces 7 ft. high, the first smelting yielding a rich 'coarse metal (55 per cent.) and a little blister-copper. Higher furnaces could not be used, on account of the large percentage of  $\text{Fe}_2\text{O}_3$ , which would have been partly reduced. The drawbacks of this smelting were the short duration of the furnace-lining (forty-seven to seventy-two hours), and great loss of metal by the slag and the flue-dust. For this reason the smelting-process was abandoned later on, and it became quite general to work up the pyrites-cinders by the wet process.

The cinders are first *finely ground*, either by crushing-rollers or by edge-runners, and at the same time mixed with a sufficient quantity of *sodium chloride*, usually in its cheapest form, viz., rock-salt. This addition, where the furnaces are worked by hand, varies from 10 to 20 per cent., on an average it is 15 per cent. But with the mechanical furnace (p. 1484) only  $7\frac{1}{2}$  salt per cent. of burnt ore is required. The ground mixture is passed through a cylindrical sieve with eight holes to the inch; the coarse particles are sent back to the mill, where they are ground down completely, so that the mixture always remains the same. The whole being finely ground, it is filled into old bogies and run on tramways over the calcining surfaces.

At Oker the cinders are mixed with 15 per cent. (formerly 20 per cent.) of Stassfurt potash salts (carnallite), and are ground down to the size of 2 mm. The Stassfurt salts contain the chlorides of magnesium, potassium, sodium, and calcium, all of which assist in the calcining-process.

Clemmer points out that, if the whole amount of cinders is ground to one size, this may cause difficulties. If too fine, a slimy mass will be formed in the tanks, which hinders the leaching-process; if too coarse, the chloridising-process and the time of leaching are too much prolonged. It is best to grind one-third to pass through a sieve  $\frac{1}{8}$ -in. mesh, and the remaining two-thirds quite fine, delivering the entire product to the furnace mixed with the salt in the mill itself. About one shovelful of salt is allowed to six of cinders.

The *calcination* or *roasting* takes place in furnaces of very different kinds. These may be classed as follows:—

1. *Ordinary reverberatory furnaces*, similar to black-ash

furnaces. These were in use at first, but have been given up long since.

2. *Reverberatory Furnaces with Gaseous Fuel.*—These were principally used at some places in Lancashire; they are illustrated by Figs. 518 to 521.

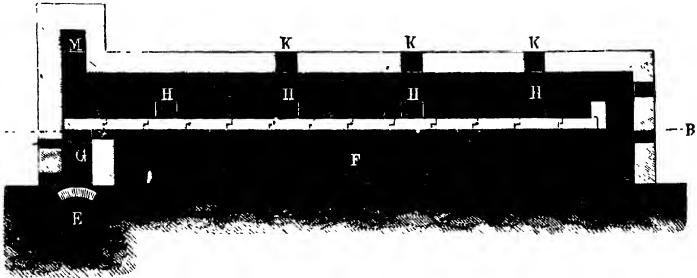


FIG. 518.

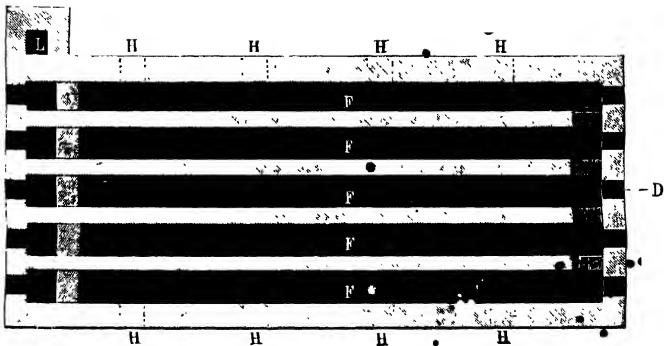


FIG. 519.

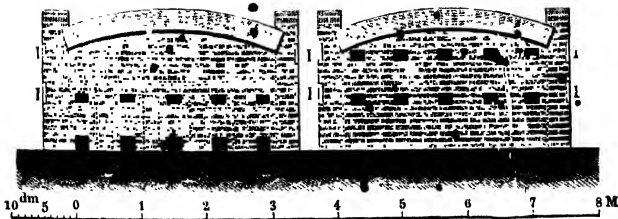
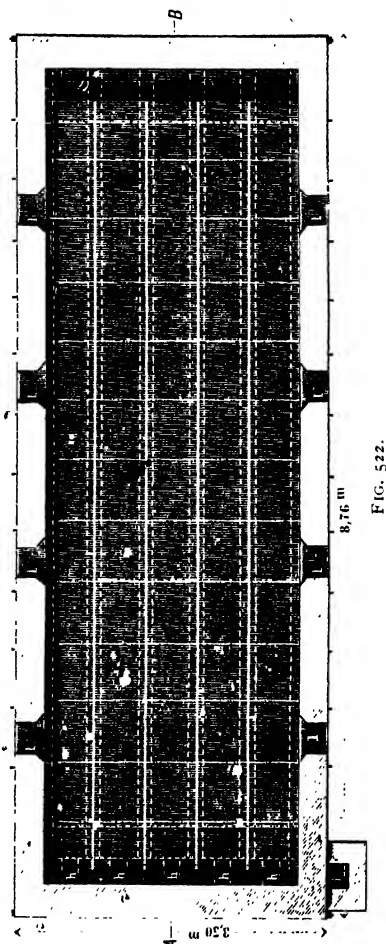


FIG. 520.

FIG. 521.

Three gas-producers furnish the gas for eight calcining-furnaces; it passes from the main flue into the flue E across the width of the furnace; from this it rises through five vertical



flues G, each of them provided with a damper; it then travels through the flues F below the furnace-bed, then directly over the charge and through the outlet M to the condensers. The

air for combustion is introduced by two tiers of holes with slides in each of the two furnace-ends (Figs. 520 and 521), so

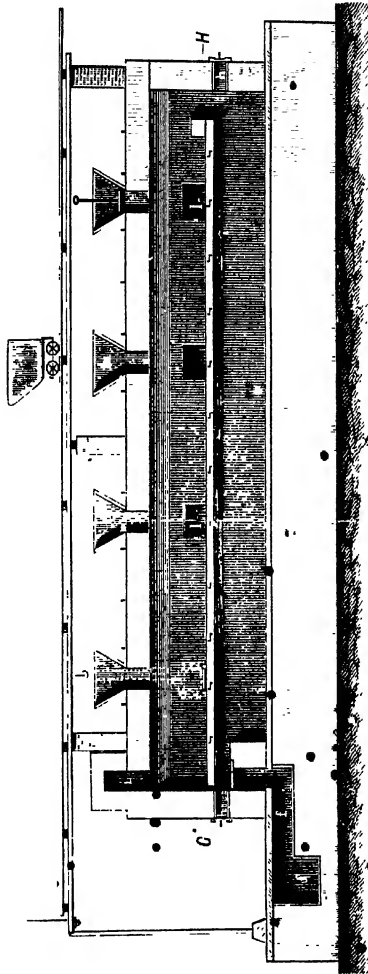


FIG. 523.

that one of the tiers communicates with the flues below the bed, the other with the space above the fire-bridge. Thus the combustion can be regulated so that some unburnt gas gets as

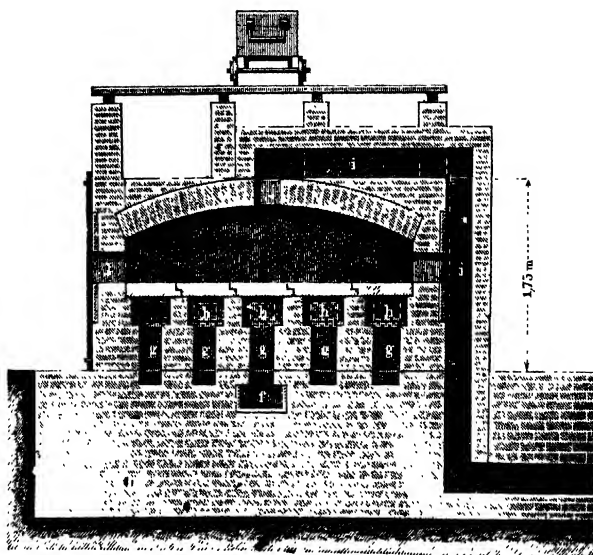
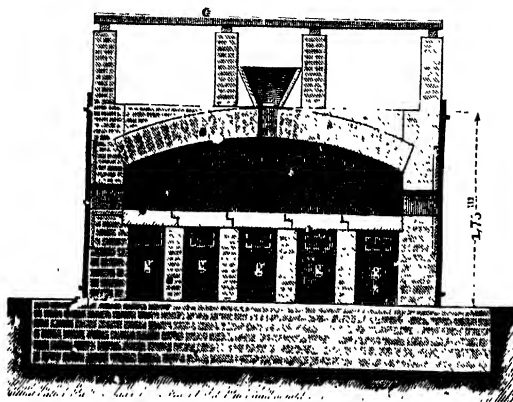


FIG. 524.



1; FIG. 525.

far as the fire-bridge and is only lighted there. H H are the working-doors; K, charging holes in the arch, closed by loose metal plates and fine ore on the top of these; I, binding-plates. Each furnace holds 45 cwt. of ore.

Similar furnaces are used at Oker; these are represented in Figs. 522 to 525. They work two charges of  $2\frac{1}{2}$  tons each every twenty-four hours. Here *f* marks the main channel for the gas; *g g*, five channels for the same below the furnace-beds; *h*, the slits for introducing the air; *i*, the outlet for the mixed fire- and calcining-gas to the condenser; *l*, the working-holes; *m*, the charging-hoppers.

3. *Blind roasters (muffle-furnaces)* are employed at all the works of the Tharsis Sulphur & Copper Company, Figs. 526 to 528. Here the flame does not come into direct contact with

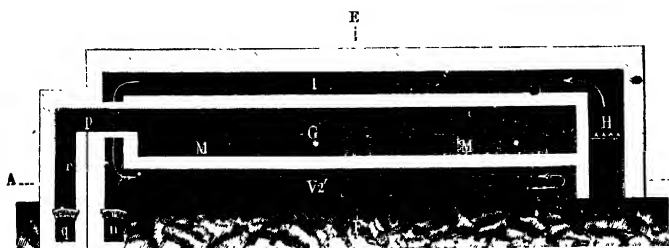


FIG. 526.

the charge, but only acts through the brickwork of the bed and the arch. The charge is worked in the muffle G, with the working- and discharging-doors M. Its bottom is formed by fireclay slabs covering the fire-flues V L; its cover by a thin arch. The ore is spread in a thin layer, and receives the air necessary for roasting it only through the working-doors M; in the other part of the furnace the oxygen contained in the fire-gas is acting as well. The flame from the double grate H first travels by I over the muffle-arch, then downwards in three channels on each side ( $V_2$  and  $V_3$ ). The gas of every three channels is united in a flue (L and L'), and, after having returned in the opposite direction, descends by *m* into the flue *n* situated below the ground-line, which enters the main chimney. *o* is the regulating-damper; *p*, the outlet for the calcining-gas, which descends by *r* to the horizontal subterranean flue *q*, and



thence arrives at the acid-condensers. The metal dish N, on the top of the furnace, serves for a first heating of the mixture; it communicates with the muffle through several pipes, usually covered with a metal plate; by raising the latter the mixture is let down into the muffle.

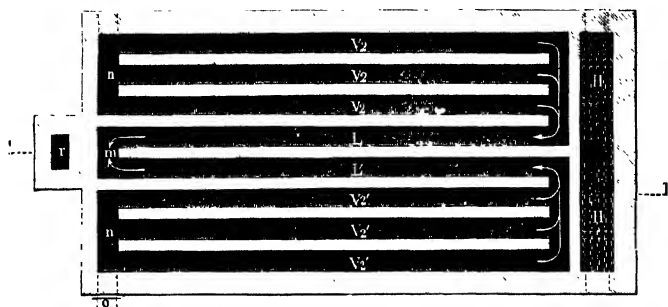


FIG. 527.

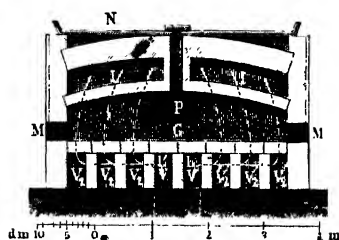


FIG. 528.

The muffle-furnaces at Natrona (near Pittsburgh) are exactly similar to the above. We therefore abstain from reproducing the design in *Min. Ind.*, ix. p. 287, and merely quote the dimensions of those furnaces. "Ash-pit 18 in. wide, 3 ft. 1 in. deep. Fire-grate 18 in. x 9 ft. Fire-bridge 2 ft. 6 in. from grates to top of muffle-arch. Space between top of muffle-arch and bottom of outer arch 14 in. (The first 6 ft. of the muffle-arch are double, the remainder only half brick.) Width of furnace-hearth 10 ft. from door to door, 7 ft. 9 in. clear (each side wall being 13½ in. thick); length 35 ft. clear; height 18 in. to spring, 30 in. to crown of arch. Pillars to

support hearth  $16\frac{1}{2}$  in. wide, 20 in. apart. Four charging-hoppers, 18 in. wide; one cast-iron gas-pipe passing through both arches, 9 in. wide.

Muffle-furnaces seem to have superseded at present all other descriptions of calcining-furnaces for this purpose.

4. *Combined furnaces*, used by the Bede Metal Company at Hebburn-on-Tyne (shown in Figs. 529 to 532). Here the flame of the fire, *a*, does not play directly upon the charge, but is

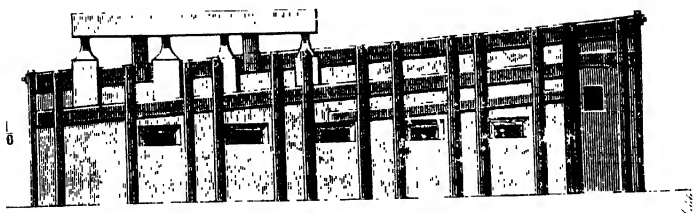


FIG. 529.

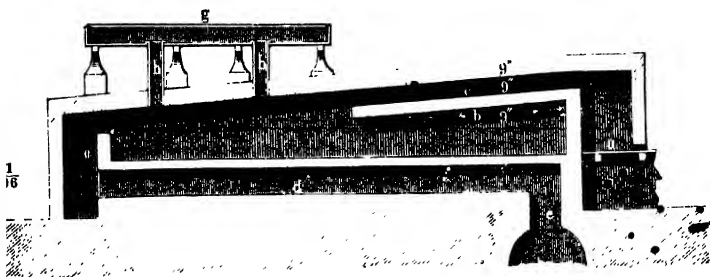


FIG. 530.

kept off it by an arch, *b*, reaching half the length of the furnace; after this the flame touches the furnace-bed directly and descends by *c* in order to return by eight channels, *d d*, beneath the furnace-bed, and to escape at *e* into an underground flue leading to an acid-condenser. The working-doors *f f* serve for stirring and discharging; the pan *g* for a first heating of the charge; the pipes *h h* for dropping it into the furnace. The purpose of the arch *b* is to avoid overheating those portions of the ore nearest the fire-bridge, in which the copper might easily

be roasted dead; in fact the hottest part of these furnaces is that behind, the part below the protecting arch hardly attaining a dark red-heat.

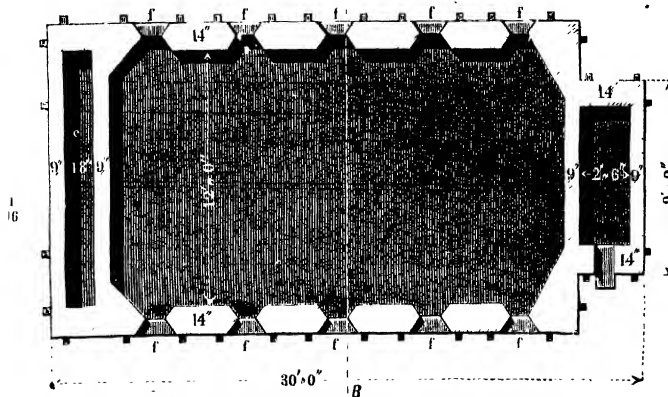


FIG. 531.

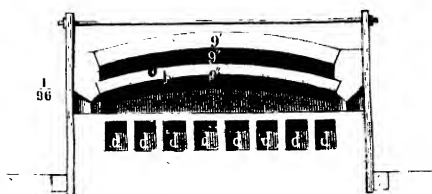


FIG. 532.

5. *Kilns*.—Buddæus (Ger. P. appl. B43222) employs for the chlorinating roasting of cinders containing Cu and Zn, in lieu of muffle-furnaces, kilns into which the cinders are introduced in the form of briquettes, made by the addition of 10 per cent. common salt, which fall into powder only when the chlorination is nearly complete.

6. *Mechanical calcining-furnaces* with revolving hearth patented in 1872 by Gibb and Gelstharpe, twelve of which were erected at the Bede metal-works. Figs. 533 to 536 represent this furnace. The bed consists of a circular pan, *bb*, made of boiler-

plate, lined with fire-bricks, D. The side walls, *m m*, and the arch, *n*, form the other parts of the calcining-space. On one side there is a fire-place, C, whose flame travels across the hearth to F, whence it enters an underground flue leading to the chimney, along with the gas evolved in calcining. The pan *b b* is carried on wrought-iron girders fixed on a central cast-iron spindle which works in a footstep and is maintained in a

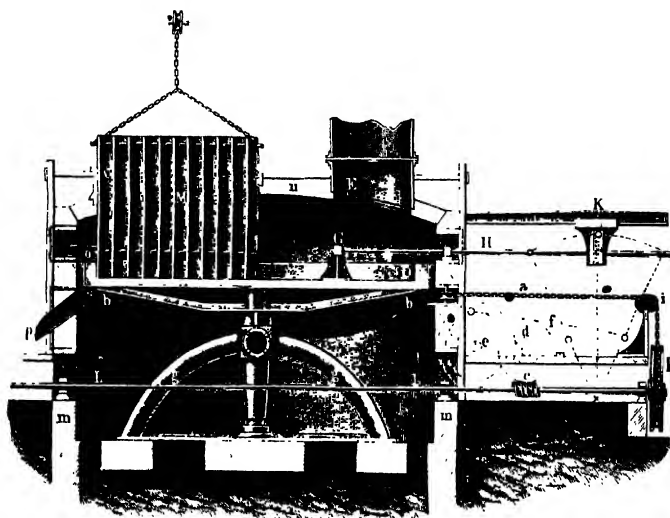


FIG. 533.

vertical position by a collar, fitted with brasses, in which an upper bearing of the spindle works, carried by the tubular cast-iron stays *g g*. This pan is caused to revolve in its own plane on the central footstep by an endless chain, *a*, carried round a sheave, *l*, from which it passes over the guiding-pulleys *i i* to the horizontal sheave underneath the pan.

A small pump, driven by the same main shaft, constantly pumps lubricating-oil from a tin vessel into the footstep, the excess of oil running back into the same vessel again. The hearth is traversed by a cast-iron plough, *G*, made to reciprocate in a radial line of the circle by the wrought-iron arm *H* connected with the cross-head *K*. The motion of this cross-



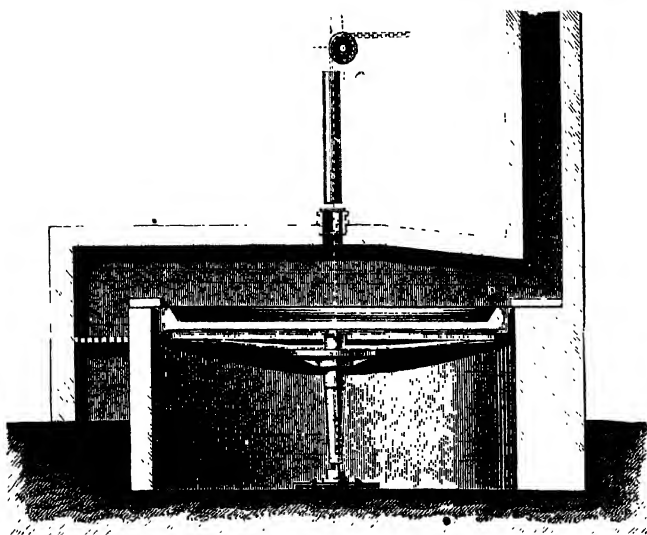


FIG. 535.

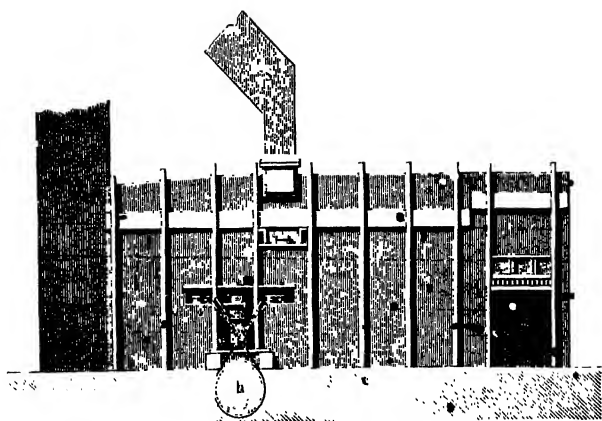


FIG. 536.

which are arranged obliquely across a radial line of the circle of the hearth on the opposite side of the centre to that in which the plough travels.' These plates are rigidly bound together at top and bottom, and suspended by a chain, so that they can be raised out of or lowered into the furnace through the roof. The plates are shown in the diagram in the position for discharging, with a plate, *o*, fixed in the doorway, folded against the outer plate of the series M. When the discharging-plates are in this position, each throws the ore carried against it by the revolution of the hearth towards the circumference into the path of the next outward plate, by which it is again thrown outwards at the next revolution, to be at length propelled against the doorway-plate, *o*, which throws it from the edge of the hearth on a shoot, *p*, over which it runs on to the floor outside the furnace. When the furnace is working, the plates are raised through the roof, and the opening through which they pass is closed by a slide. The bolt N fixes the plates in their position.

In order that the pan may freely revolve round the spindle the side walls *m m* are 1 in. apart from the edge of the pan; the air rising in this intermediate space causes the oxidation. The brickwork reaches down to the ground-line; and the machinery underneath the hearth is only accessible by an iron door, so that it is protected from the coal- and ore-dust. Every part of the machinery is very strong and not liable to get out of repair—excepting the cast-iron plough, G, which must be replaced once a fortnight, but this costs less than the tools in a furnace worked by hand. The plates M suffer very little, because they are only for a very short time exposed to the fire. The twelve furnaces at the Bede metal-works are driven by two steam-engines of 18 indicated horse-power each.

Ramén and Besköw (of Helsingborg, Sweden) have constructed a mechanical furnace for the chlorinating roasting of pyrites-cinders containing copper (and silver), patented as B. P. 23108 of 1909 (Ger. P. 242310). Upon this furnace I have received the following information from the inventors. The furnace consists of two compartments, one of which serves for the direct preheating of the mixture by producer-gases, and the other for the chlorination by means of the heat coming

from the first compartment, and by the heat developed by the reaction itself. It has been found that by the chlorinating-process so much heat is set free that the reaction needs only to be started by the assistance of external heat, and then goes on by itself. The temperature in the preheating compartment is from  $200^{\circ}$  to  $300^{\circ}$  C., that in the chlorinating compartment from  $500^{\circ}$  to  $600^{\circ}$ . The gases escaping from the preheating compartment contain only traces of acid gases and vapours, and can be mostly passed at once into the chimney; by means of special arrangements they are prevented from getting into the chlorinating compartment. Hence concentrated gases are obtained from the latter, and the air can fully develop its oxidising influence. The heat economy is much better than in muffle-furnaces, and no local overheating can take place, so that the mixture of common salt and ore nowheres fluxes, and the mechanical stirring is not impeded by the formation of crusts on the stirring-blades and the furnace walls, which frequently occurs in furnaces heated from without, and has led to the nearly universal employment of hand-worked furnaces in the European copper works. In its most recent form the furnace works up 40 to 45 tons of cinders in twenty-seven hours, with an expenditure of 1.6 to 2 per cent. coal (against 15 per cent. in hand-worked furnaces); one man can attend to one or two furnaces. The calcined mass contains less insoluble copper than that from hand-furnaces. The inventors calculate a saving of at least 3s. per ton against hand-furnaces, exclusive of capital interest and amortisation. According to a communication received from them in April 1912, already twenty-seven of these furnaces were at work at Helsingborg, Duisberg, Hamburg, Runcorn, Glasgow, etc., and another five furnaces were being built. The above furnaces work about 550,000 tons cupreous pyrites-cinders, *i.e.*, about half of the quantity submitted to chlorinating roasting in Europe, and they can deal with cinders and ores of such low copper content (down to 0.7 per cent.) as formerly did not pay working for chlorinating roasting. The ores treated in this way can be charged directly into blast furnaces without any admixture of other ores.

*Process of Working the Furnaces.*—All these different descriptions of furnaces have the same object; and the style of working



is accordingly very similar in all cases. The ore must, of course, be completely roasted—that is, sufficiently to convert the copper into sulphate, which, owing to the presence of sodium chloride, at once forms with this, by mutual decomposition, cupric chloride and sodium sulphate; whilst the iron should be converted as completely as possible into ferric oxide, so as to become insoluble. In this process, owing to the simultaneous action of  $\text{SO}_2$  and  $\text{O}$  upon  $\text{NaCl}$ , chlorine is evolved, which must greatly aid in chlorinating the copper as well as any other metal present. At the same time a large quantity of  $\text{HCl}$  is formed, which converts the oxides of copper, silver, zinc, etc., into chlorides, whilst at the calcining-temperature ferric chloride cannot continue to exist as such. At Oker the formation of hydrochloric acid is purposely promoted by using carnallite in lieu of common salt, as the  $\text{MgCl}_2$  contained in the former readily yields  $\text{MgO}$  and  $\text{HCl}$ . This, however, is not absolutely requisite, as with  $2\text{NaCl}$  the  $\text{CuSO}_4$  already produced in calcining yields  $\text{CuCl}_2$  and  $\text{Na}_2\text{SO}_4$ .  $\text{Cu}_2\text{Cl}_2$  also is always formed at the same time. Since the chlorides of copper are both unstable and volatile at very high temperatures, a low red-heat ought not to be exceeded; so that any copper-pyrites still present in the cinders is not burnt, and therefore escapes chlorination. Accordingly, copper-pyrites (or  $\text{Cu}_2\text{S}$ ) ought not to be present in any quantity for the wet-extraction process; and consequently ores with more than 8 per cent. of copper, which can never be roasted with sufficient completeness in the chemical factories, cannot be utilised by this process, but only by smelting.

Manifold experience has taught that without employing common salt (that is, without chlorinating) it is never possible, even approximately, to hit the point where the more easily decomposed ferric sulphate no longer exists, whilst the less easily decomposable cupric sulphate is still present as such, the iron being then present in an insoluble, the copper in a soluble form. If ferric salt remains in a soluble form, it naturally passes over into the lyes, and, in the operation of precipitating the copper, causes a great loss of metallic iron by its reduction to ferrous salts. If, on the other hand, much copper has likewise passed into an insoluble form, more hydrochloric acid is required for its solution. In any case the formation of some

cupric oxide and cuprous chloride, insoluble in water, cannot be avoided.

Wedding has observed, and described in detail, the calcining-process as carried on at Widnes in a gas-furnace. The charge, of 45 cwt. of ore mixed with 17 per cent. of salt, is let down on to the hearth, spread out and slowly heated till a low red-heat has been reached nearest the fire-bridge; the charge is turned over and left to itself, the gas being shut off, but the air being allowed to enter, so that after two hours scarcely any glowing can be perceived at the fire-bridge. After one hour's and three hours' calcining respectively, the copper of the charge behaved as follows:—

	1 hour's calcining.	3 hours' calcining.
	Per cent.	Per cent
Soluble in water . . . .	54	51
" HCl . . . .	38	42
" NO <sub>2</sub> H . . . .	8	7

After three hours the charge is quite dark, and is now well turned over with a slice of 3 or 4 in. breadth, as well as with a rake; there ought to be no necessity for giving more fire, as the temperature should from the first have been raised to the proper point. On raking over the charge, which is done regularly with short interruptions only, the temperature rises of itself in consequence of the chemical reactions, the rise becoming sensible after four and three-quarter hours (counting from the beginning); so that after five and a quarter hours a dark red-heat has been reached. Up to this point there is a copious evolution of white vapours and blue flames; from this period there is less of these, and it is the calciner's principal task to see that the heating of the charge is quite equal all over, and that some places do not show more blue flames than others. After six and a half hours these flames almost entirely disappear; and this fact, together with the greenish-grey colour of the charge, constitute the practical tests for judging whether the operation is finished. A sample is now drawn; and if its examination shows that the calcining-process is complete, the charge, which

has now been six and a half or six and three-quarter hours in the furnace, is drawn out. Of the copper now—

75	per cent.	is soluble in water,	
20	"	"	HCl,
5	"	"	NO <sub>3</sub> H.

Good workmen can finish the calcining in a gas-furnace in six hours.

Wedding observes that the samples dissolved in water constantly show more sulphur, and that the testing of the calcined ore of different works proves the process to be carried out very unequally; but it is certain that the best results are in fact got by the most careful work. The calciner's task is, first to heat the charge and thus to start the chemical reactions, but then to maintain these at the lowest possible heat up to the finish, and to spread them equally through the whole mass. It is of great importance not to leave the ore any longer in the furnace than is exactly necessary; this is made difficult by the depth of the layer of ore, viz., 5 or 6 in.—which, on the other hand, facilitates the chlorination, since the gas rising in the ore heated both at top and bottom has all the more opportunity of coming into contact with all parts of it.

Evidently the process is altogether dependent upon the skill of the workman, whilst with the mechanical furnace of Gibb and Gelstharpe (p. 1484) only the firing needs attention. In the latter furnace indeed a lower heat is sufficient, one that never reaches a red glow visible in daylight.

At Oker, where gas-furnaces exactly like those of Widnes are used, each charge of 50 cwt. of ore with 15 per cent. potash salts is brought to a low red-heat in four hours; the firing is then interrupted and the mass raked over. Owing to the chemical reactions, the heat at first increases, but towards the end goes back again. During the turning-over stage, which lasts five hours, the air-slides are opened to admit the air to the charge; after that time the charge is drawn. Two charges are put in every twenty-four hours. Analysis of a sample taken in the middle of the calcining-process (the mixture containing 20 per cent. carnallite):—

Soluble in water.				Insoluble in water.			
	Per cent.		Per cent.		Per cent.		Per cent.
Cu	1.94	Calc. as $\text{CuCl}_2$	3.11	Cu	4.32	Calc. as $\text{CuO sol. in HCl}$	5.12
Ag	0.003	" $\text{AgCl}$	0.004			$\text{Cu}_2\text{S sol. in aqua regia}$	0.29
Fe	0.74	" $\text{FeCl}_2$	1.68	Pb	0.39	" $\text{PbSO}_4$	0.57
$\text{Al}_2\text{O}_3$	0.11	" $\text{Al}_2(\text{SO}_4)_3$	0.39			" $\text{Fe}_2\text{O}_3$	45.38
Mn	0.69	" $\text{MnCl}_2$	1.58	Fe	34.49	" $\text{Fe}_2(\text{SO}_4)_3$	3.27
Ni	0.20	" $\text{NiCl}_2$	0.44			" $\text{FeS}_2$	2.64
Zn	1.60	" $\text{ZnCl}_2$	3.40	$\text{Al}_2\text{O}_3$	3.30	" $\text{Al}_2\text{O}_3$	3.30
CaO	2.76	" $\text{CaCl}_2$	6.27	Mn	0.03	" $\text{Mn}_2\text{O}_3$	0.04
MgO		" Sulphates	18.15	Zn + Ni	0.29	" $\text{ZnO} + \text{NiO}$	0.36
$\text{K}_2\text{O}$				CaO	0.45	" $\text{CaSO}_4$	1.09
$\text{Na}_2\text{O}$				$\text{SO}_3$	1.86		
				S	1.47		
				Cl	trace		
				Insoluble in acids			2.96
			35.024				65.02

Sample of calcined ore taken at the finish:—

Soluble in water.				Insoluble in water.			
	Per cent.		Per cent.		Per cent.		Per cent.
Cu	3.86	Calc. as $\text{CuCl}_2$	8.17	Cu	2.57	Calc. as $\text{CuO}$	3.18
Ag	0.005	" $\text{AgCl}$	0.006			$\text{Cu}_2\text{S}$	0.03
Fe	0.60	" $\text{FeCl}_2$	1.38	Pb	1.17	" $\text{PbSO}_4$	1.26
$\text{Al}_2\text{O}_3$	0.17	" $\text{Al}_2(\text{SO}_4)_3$	0.56			" $\text{Fe}_2\text{O}_3$	47.91
Zn	1.64	" $\text{ZnCl}_2$	3.42	Fe	34.56	" $\text{Fe}_2(\text{SO}_4)_3$	1.02
Mn	0.75	" $\text{MnCl}_2$	1.71			" $\text{FeS}_2$	1.18
Ni	0.07	" $\text{NiCl}_2$	0.15	$\text{Al}_2\text{O}_3$	0.44	" $\text{Al}_2\text{O}_3$	0.44
CaO	1.60	" $\text{CaCl}_2$	3.17	Zn	0.37	" $\text{ZnO}$	0.46
MgO		" Sulphates	20.50	Ni + Ni	trace	" $\text{CaSO}_4$	1.09
$\text{K}_2\text{O}$				CaO	0.49		
$\text{Na}_2\text{O}$				$\text{SO}_3$	1.49		
				Cl	trace		
				S	0.64		
				Insoluble in acids			3.69
			39.066				60.36

The mechanical furnace has the advantage also in respect of the addition of salt; only  $7\frac{1}{2}$  per cent. of salt is required in it, against 15 in the hand-furnaces. Often only a portion of the salt is mixed with the ore at the outset, and the remainder added afterwards. In the blind roasters the ore

is calcined first nine hours with 12 per cent. salt, and another three hours with 8 per cent. more salt. In the combined furnaces with protecting arch the weight of ore is 58 cwt., and the time of calcining eight hours; in the mechanical furnaces 5 tons and nine hours.

Gibb gives the following analyses of the results of calcination:—

	Gas furnace.		Close furnace.		Mechanical furnace.	
	Per cent.	Cu Per cent.	Per cent.	Cu Per cent.	Per cent.	Cu Per cent.
Cupric chloride .	4.03	= 1.90	4.25	= 2.00	6.70	= 3.15
Cuprous chloride .	0.32	= 0.20	0.35	= 0.21	...	
Cupric oxide .	1.26	= 1.00	0.88	= 0.70	0.32	= 0.25
Sodium sulphate .	2.50		3.40		0.90	
Insoluble copper .	13.18		17.40		14.03	
		.15		0.12		0.13
Total copper .		3.25		3.03		3.53

The principal point is always this, that as little copper as possible should remain in a state insoluble in water and dilute acids. In the above cases the quantity varies from 0.12 to 0.15 per cent.; the slightly more favourable result of the blind roaster, according to Gibb, is far more than counterbalanced by its greater consumption of fuel (50 to 100 per cent.). The most favourable result is obtained with the mechanical furnace, in which next to no cuprous chloride and, even with the worst ores, rarely more than 0.25 per cent. of CuO are formed.

At Oker the average result of the constantly taken samples of calcined ore is: 75 per cent. of the copper contained in the ore is soluble in water, 20 per cent. in dilute hydrochloric acid, and 5 per cent. in aqua regia.

If the pyrites contains more than 4 per cent. copper, the cinders cannot be worked in England with advantage by the wet process. At the Bede metal-works many experiments have been made with richer ores; but with 6 per cent. copper the salt, the coals, and the labour are too dear. In this case, however, another circumstance comes into play: by the Cornish copper assay about 2 per cent. copper less than the truth is indicated; and this with a poor ore of course amounts to a much larger proportion of the whole (sometimes more than

half) than with richer ores; thus the former are cheaper for the wet process than the latter. At Oker, where this reason does not exist, ore up to 8 per cent. Cu can be extracted by the wet process.

It has already been remarked that the sulphur in the cinders must bear a certain proportion to the copper; with a 4 per cent. ore it ought not to exceed 6 per cent.; an equal percentage of S and Cu is preferable. If less S is present, raw pyrites must be added. The more S there is present, the more salt must be added, and the more time will the calcination take.

The *tests* for ascertaining the completion of the calcination are of a very simple character, which is the more necessary as they must be made very quickly. A certain measure of the charge, not weighed, is lixiviated by water and dilute HCl, just as on the large scale; the residuc is boiled with aqua regia, supersaturated with ammonia, and allowed to settle; the more or less blue colour of the solution of ammonio-cupric salt gives a sufficient indication of the percentage of insoluble copper.

*Other Processes.*—Richard (*Chem. Zeit.*, 1908, pp. 5-7) discusses the way of roasting cupreous ores and cinders so as to obtain the maximum yield of soluble copper salt. This takes place with the increase of ferric sulphate; hence the roasting should be performed at a temperature where this is possible. The finer the grain of the ore, the better for this purpose; 2 mm. should not be exceeded. It is most useful to treat the roasted ore in the furnace itself with a few per cent. of sulphuric acid. During the last period of roasting the traces of Au and Ag present can be made soluble by suitable additions, and the liquors can be worked directly for cupric sulphate. Or also by precipitating the Cu by Fe, final liquors can be obtained which can be worked for red and black iron paint. The residue from lixiviation goes to the iron-smelting establishments.

Parent (Fr. P. 411863) calcines pyrites-cinders in a special hearth on the top of the burner, or on the uppermost shelf of the burner, after mixing them with dilute sulphuric acid or finely powdered pyrites; in one or two hours the copper is completely soluble. In an addition he claims the employment of ferrous and ferric sulphate and sulphuric acid for mixing with the cinders, and the employment of two charging-hoppers,

one for feeding the sulphating hearth on the top and the other for delivering material to be desulphurised to the hearth below.

Kothny (*Chem. Zeit. Rep.*, 1911, p. 457) finds temperatures between  $500^{\circ}$  and  $600^{\circ}$  as most appropriate for the calcining of pyrites-cinders with salt.

*Condensation of the Calcination-gas.*—In all the descriptions of furnaces mentioned above, except the blind roasters, this gas is mixed with the fire-gas, but even in these it is mixed with air to such an extent that a condensation of strong acid is not very well possible. The acid obtained is a little more concentrated than that from open calciners; but this matters very little, as it is always used in a very dilute state for lixiviating. The calcination-gas principally contains (besides oxygen and nitrogen)  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HCl}$ ,  $\text{Cl}$ , and very small quantities of metallic chlorides. Henderson had proposed to volatilise the copper entirely as  $\text{CuCl}_2$ , and condense the latter in towers; but this has turned out quite impracticable. The small quantity of copper passing over into the condensers, about  $\frac{1}{4}$  per cent. of the whole, is not lost, as the condensed acid is used for lixiviating the charge.

The condensation of the gas from the calciners takes place in towers of exactly the same kind as those for hydrochloric acid (described in detail in our second volume)—that is to say, made of brickwork set in tar and sand (or, better, of stone flags), and packed with coke, fire-bricks, and the like. Sometimes condensers made of very large stoneware pipes are employed. Coke packing can be used with blind roasters; but the other furnaces require condensers packed with bricks or stoneware, and of greater dimensions, as they have to serve for a larger volume of gas. The size of the condensing-towers varies with that of the plant; for twelve furnaces a tower of 8 ft. square and 40 to 50 ft. high is sufficient. The gas enters at the bottom, meets a spray of water coming from the top, which washes the acids out of it, and leaves the tower at the top, whence it is taken downwards into a flue leading into the chimney.

The total condensed liquid (a mixture of weak sulphuric and hydrochloric acids; the  $\text{SO}_2$  in the condensation is oxidised to  $\text{SO}_4\text{H}_2$  by the action of the chlorine) is used in the succeeding operation of lixiviating the calcined mass, and frequently is not even sufficient for dissolving all the  $\text{CuO}$  and  $\text{Cu}_2\text{Cl}_2$ .

*Lixiviation of the Calcined Charge.*—This is carried in bogies running on tramways over each of the lixiviating-tanks and tipped into these. The only available material for the tanks, is wood; most metals are excluded by the nature of the lixiviating-liquid; stone, asphalt, etc., both by their costliness and by the heat of the charge. As such large wooden vessels cannot well be kept tight on account of the unavoidably rough treatment and the hot acid liquors, the whole floor of the lixiviating-shed is covered with a thick layer of asphalt and slopes to one side, so that all liquors leaking out run off to a catch-well, into which enter at the same time earthenware spouts for carrying the strong copper-liquors.

The lixiviating-tanks are square, about 11 × 11 ft. wide and 4 to 5 ft. deep, made of well-seasoned and planed 3-in. planks kept together by corner-pieces, screw-bolts, etc. The joints are tightened by putting on a little red-lead before putting the planks together; the bottom joints are besides caulked with tarred spun yarn, and the whole vessel is painted with hot coal-tar. At Oker lead-lined vessels are used, which are very expensive and frequently need repairing. On the bottom, laths on end are placed; upon these, perforated fire-tiles or boards; upon this false bottom a layer of sifted furnace-cinders is spread out; and on the top is put a layer of heather or coke (at Oker of straw) 3 to 6 in. deep. The liquors are conveyed in earthenware and india-rubber tubes of 3 to 4 in. diameter, the latter provided with iron pinch-clamps. In order to force the liquors from one tank to the other, or from the catch-well into the tanks, simple stoneware injectors are provided. Each tank is provided with a steam-pipe for heating.

At Natrona the leaching- and precipitating-tanks are made of very sappy yellow pine, well tarred before use, and consist of an outer shell of 3-in. planks and an inner lining of the same thickness, leaving a 3-in. space between the two layers of timber, which space is afterwards filled with a mixture of "hard tar" (probably soft pitch) and screened sand, melted together in a kettie and well mixed before pouring in. The bottom is covered with a 3-in. coat of the same material. The planks are put together with wooden pins and bound, as shown in Fig. 537. The ends or joints are halved together, and caulked with oakum and red-lead. The tanks are 12 × 12 ft., 4 ft. or 6 ft.



deep. In lieu of a grating, hard-burned bricks are laid flat side by side. Fig. 538 shows the wooden spigot serving in lieu of an outlet-cock.

Into every tank about 10 tons of calcined ore are put, quite hot from the furnaces, and are first covered with weak liquor

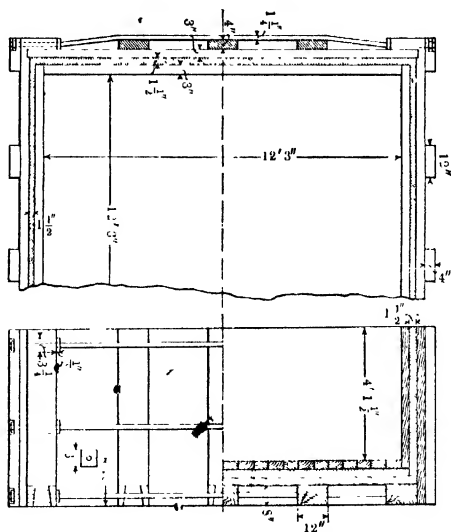


FIG. 537.

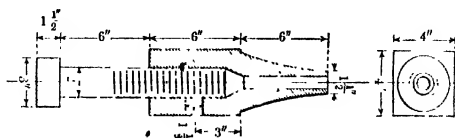


FIG. 538.

from a previous operation, which gets heated by the heat of the mass itself. After one or two hours the now concentrated liquor is run off by a plug-hole below the false bottom, and is now ready for precipitation. The plug is put in again, and the lixiviation continued by hot water; thus weaker liquors are produced, which are forced to a fresh tank as just described. Generally three waters are put on, and thus most of the purest copper and 95 per cent. of all the silver contained in the pyrites are obtained. Then follow several (up to six) washings with

the weak condenser-acid, or, if this does not suffice, with hydrochloric acid bought for the purpose and much diluted. This is not necessary in the case of mechanical furnaces, because the copper-salts from these are mostly soluble in water; but it is generally necessary with hand-furnaces. Even when no acid need be bought, but sufficient condenser-acid is obtainable, a saving of acid is important, since the condenser-acid conveys arsenic and bismuth into the copper.

The liquors obtained by the use of acid contain many impurities, especially As, Bi, Sb, and Pb—according to Gibb, for every 100 parts of Cu, 5.4 As and 0.3 Bi; and they are accordingly treated separately in most works, because they yield impure copper.

It is a principal rule to allow each water to stand only a few hours on the ore; the nine washings of each tank, together with charging and emptying it, are not to last beyond forty-eight hours. Accordingly, for every 5 tons of calcined ore obtained per diem one tank is required, and besides, on the whole, a few reserve tanks.

The *residue from lixiviation*, after draining, is tipped on a heap and afterwards sold to the iron-smelters. It is the value of this residue which makes the wet process in this case more profitable than the dry process, as that residue is a valuable iron-ore, going by the name of *purple ore* or *blue billy*. The following is the composition of two average samples:—

Ferric oxide . . .	90.61	95.10
Copper . . .	0.15	0.18
Sulphur . . .	0.08	0.07
Phosphorus . . .	...	...
Lead sulphate . . .	1.46	1.29
Calcium sulphate . . .	0.37	0.49
Sodium sulphate . . .	0.37	0.29
Sodium chloride . . .	0.28	...
Insoluble . . .	6.30	2.13
	99.62	99.55
Metallic iron . . .	63.42	60.57

This ore is thus shown to be very rich in iron, entirely free from phosphorus, and to contain very little sulphur; its slight percentage of copper does no harm. The only drawback is its fine state of division. It can be to some extent employed directly in its pulverulent state as a mixture with 5 or even

only 3 parts of lump iron-ore in blast-furnaces; using limestone in addition, both grey and white pig can be made from it. Most of the purple ore, however, is used for "fettling" the sides and bottom of puddling-furnaces in lieu of hematite, for which it is very well adapted, or in the Siemens-Martin process. Its direct conversion into iron and steel on the large scale has not yet been carried out. At Oker it is easily used up in the various metallurgical processes there carried on, and even its small percentage of copper is turned to account. They obtain thereupon 130 parts of pyrites-cinders, 75 parts of extraction-residues of the following composition:—

	Per cent.
Ferric oxide . . . .	79.0
Alumina . . . .	3.0
Magnesia and alkalis . . . .	1.0
Lime . . . .	2.5
Sulphuric acid . . . .	5.5
Insoluble in acids . . . .	6.0

Purple ore is more valued the freer it is from siliceous gangue; and for this reason that made from Spanish and Portuguese is preferred to that from Norwegian pyrites.

According to Clemmer (*Min. Ind.*, ix. p. 289) the purple ore is moulded in America into briquettes (it is not stated with what agglomerating substances) by an ordinary automatic brick-making machine and burned in a down-draught kiln. These briquettes test less than 0.25 per cent. sulphur, and are easily disposed of to pig-iron manufacturers, some of whom require all the sulphur to be removed; for this purpose the briquettes must be burned at a very high temperature for five or six days and virtually fused.

*Cf.* p. 1457 as to the various processes for agglomerating pyrites-cinders, all of which of course apply also to purple ore.

The *leall* contained in the pyrites is found in the cinders as sulphate. Part of this is carried away with the leaching-liquors in the shape of mud and is removed by settling out; this mud contains some gold. Another portion remains behind in the lixiviated residue, mixed with the purple ore and injuring its quality as an iron-ore. Schaffner (*Fischer's Jahresber.*, 1880, p. 136) removed and utilised the lead in the following simple and cheap manner:—After roasting the ore with common salt as

usual and washing out all soluble chlorides and sulphates, the residue is drenched with chloride-of-calcium liquor (from the Weldon chlorine process) of 9° to 12° Tw., heated to about 40° C., and acidulated with hydrochloric acid. By mutual decomposition gypsum and lead chloride are at once formed which remain dissolved in the acid liquor. This is run off and brought into contact with metallic iron, which precipitates the lead in the metallic state. After washing, the purple ore is quite free from lead sulphate. At the same time the  $\text{CaCl}_2$  dissolves the last traces of copper and silver present as  $\text{Cu}_2\text{Cl}_2$  and  $\text{AgCl}$ ; these are precipitated together with the lead. It should be noticed that sulphuretted hydrogen fails to indicate the lead in a solution of  $\text{PbCl}_2$  in  $\text{CaCl}_2$  acidulated with  $\text{HCl}$ .

Where the copper is precipitated by spongy iron, a portion of the purple ore is employed for preparing the latter.

*Copper-liquor obtained by Lixiviation.*—The effect of the lixiviation is best seen from the following analyses by Gibb, which at the same time illustrate the great difference of work between mechanical and hand-worked furnaces:—

	Mechanical furnace ore.		Hand-worked furnace ore.	
		Copper.		Copper.
	Per cent.	Per cent.	Per cent.	Per cent.
<i>Soluble in water—</i>				
Cupric chloride . . . . .	4.16	1.96	3.81	1.82
Cuprous chloride . . . . .	...	...	0.19	0.12
Cupric sulphate . . . . .	1.83	0.81	...	...
Ferrous sulphate . . . . .	0.15	...	...	...
Ferric sulphate . . . . .	0.75	...	...	...
Zinc sulphate . . . . .	2.01	...	1.95	...
Calcium sulphate . . . . .	1.29	...	1.39	...
Sodium sulphate . . . . .	9.07	...	11.13	...
Sodium chloride . . . . .	...	...	2.64	...
<i>Soluble in dilute hydrochloric acid—</i>				
Cuprous chloride . . . . .	0.015	0.01	0.33	0.21
Cupric oxide . . . . .	0.225	0.18	1.01	0.81
Lead sulphate . . . . .	} not determined		} not determined	
Ferric oxide . . . . .				
<i>Residue (by difference) —</i>				
"Purple iron-ore" . . . . .	80.40	0.08	77.55	0.11
	100.00	3.04	100.00	3.07
Sodium chloride equivalent to sodium salts as above . . . . .	7.56		11.81	

The composition of the copper-liquor, according to Gibb, is, in grammes per litre:—

	From hand-worked furnaces		From mechanical furnaces.
Sodium sulphate . .	144.1	Sodium sulphate . .	110.9
Sodium chloride . .	63.9	Sodium chloride . .	4.1
Chlorine in combination with heavy metals . .	67.1	...	...
Copper . . . .	53.0	Cuprous chloride . .	53.2
Zinc . . . .	6.9	Cupric chloride . .	0.8
Lead . . . .	0.6	Zinc sulphate . .	10.1
Iron . . . .	0.5	Lead sulphate . .	0.8
Calcium . . . .	0.7	Ferrous sulphate . .	4.3
Silver . . . .	0.047	Calcium sulphate . .	5.0
		Silver . . . .	not estimated

At Oker the process was formerly carried out in the following way.<sup>1</sup> The calcined charge is lixiviated in parcels of 5 tons each, first with the final liquor, which is always regenerated in the process. One hundred parts of the latter, of 1.145 sp. gr., contained:—

	Per cent.		Per cent.
Cu . . . .	0.015	CoO + NiO . . . .	0.01
Pb . . . .	trace	CaO . . . .	0.12
FeO . . . .	2.14	MgO . . . .	0.52
Fe <sub>2</sub> O <sub>3</sub> . . . .	0.75	Alkalies . . . .	2.61
Al <sub>2</sub> O <sub>3</sub> . . . .	0.11	Cl . . . .	2.56
ZnO . . . .	0.06	SO <sub>3</sub> . . . .	5.89
MnO . . . .	0.31	As + Sb . . . .	trace
Total solids . . . .	14.495 per cent.		

This liquor, already heated in pumping by the injector to 50° C., is further heated, when it comes into contact with the calcined charge, by the solution of the anhydrous salts, of course also by the heat of the charge itself, nearly up to the boiling-point, by which the solution is assisted. When the charge is perfectly penetrated by the final liquor, the outlet-tap is opened and fresh final liquor runs in as long as the copper-liquor running away at the bottom still shows a blue colour.

<sup>1</sup> This process is still described here, as it may be of use in analogous cases; but it has now been discontinued at Oker, the character of the copper-ores having changed, so that they cannot be subjected to the wet-extraction process.

This first period lasts four or five hours, and furnishes a copper-liquor of 1.355 sp. gr., and of the following composition:—

	Per cent.		Per cent.
Cu . . .	3.71	CoO + NiO . . .	0.04
Pb . . .	0.01	CaO . . .	trace
Ag . . .	0.005	MgO . . .	0.27
Bi . . .	trace	Alkalies . . .	10.60
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> . . .	0.29	Cl . . .	12.56
ZnO . . .	4.97	SO <sub>3</sub> . . .	8.95
MnO . . .	0.58	As + Sb . . .	0.32
Total solids . . .	42.305 per cent.		

After the first lixiviation is over, the dilute condenser-acid, first brought to boiling, is run into the tanks and allowed to act for twenty-four hours; then it is run off, and a third lixiviation is effected by dilute sulphuric acid. For 5 tons of ore 2½ cwt. of chamber-acid of 106° Tw., diluted to 12° Tw. and heated to the boiling-point, is employed, and allowed to remain in contact with the ore for two days, or until the liquor acquires a neutral reaction. Its analysis showed:—

	Per cent.		Per cent.
Cu . . .	0.58	CaO . . .	0.07
Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> . . .	2.13	MgO . . .	0.04
ZnO . . .	0.06	Alkalies . . .	0.62
MnO . . .	0.12	Cl . . .	0.13
CO + Ni . . .	0.02	SO <sub>3</sub> . . .	2.39
Total solids . . .	6.160 per cent.		

The first copper-liquors contain most of the silver, and are therefore kept apart from the later liquor, poorer in this respect.

The cupric chloride is, of course, easily dissolved in the final liquor; the cuprous chloride in the presence of alkaline chlorides is also dissolved at a higher temperature without difficulty; lastly, cupric oxide should be converted into CuCl<sub>2</sub> and Cu<sub>2</sub>Cl<sub>2</sub> by the FeCl<sub>2</sub> of the final liquor, and become soluble thereby ( $2\text{FeCl}_2 + 3\text{CuO} = \text{Fe}_2\text{O}_3 + \text{Cu}_2\text{Cl}_2 + \text{CuCl}_2$ ); but this could only be done by an intimate mechanical mixture of the liquor with the ore, and it is therefore preferred to dissolve merely 75 to 80 per cent. of the copper by means of the final liquor, and the remainder by further lixiviations with dilute acids. In Bräuning's paper no hint is given as to the way in

which the increase of impurities in the final liquor is prevented. No doubt only a portion of it is taken back into use and another portion run to waste; so that there must always be a partial renewal.

Glendinning (B. P. 8602 of 1885) converts the cuprous chloride in the liquors into the cupric salt by blowing in air, in the presence of at least 2 mol. of free HCl to one of salt, together with not less than  $3\text{FeCl}_2$  to  $2\text{Cu}_2\text{Cl}_2$ . [It seems certain that in consequence of this process the solution will require the addition of much more iron than before.] If arsenic be present, the excess of free HCl is to be removed by alkali or CuO; in this case, when passing air through the liquid, most of the arsenic will be precipitated in combination with  $\text{Fe}_2\text{O}_3$ .

Rawson (*Chem. News*, xlix. p. 161) describes a method for estimating cuprous chloride in copper-liquors by means of potassium permanganate.

*Precipitation of the Copper from the Liquors.*—This is sometimes preceded by a special treatment for obtaining the silver, which will be subsequently described. The precipitation of the copper now takes place everywhere by means of metallic iron, since the ingenious process of Gibb and Gelstharpe has been abandoned. It consisted in precipitating the copper by sulphuretted hydrogen, which was recovered at a later stage of the process: the precipitated cupric sulphide was washed and pressed in a filter-press, and smelted in furnaces in the usual way into "coarse metal." The acid mother-liquors, containing the whole of the sodium sulphate, were evaporated to dryness in a furnace, mixed with small coal and reduced in another furnace; thus a mass containing nearly 35 per cent. of sodium sulphide and 2.4 per cent. of sodium carbonate was obtained. This was lixiviated with hot water; the solution was systematically treated with impure carbonic acid, obtained by burning coke; and thus on the one hand sulphuretted hydrogen was given off, which served for precipitating the copper in the first stage of the process; on the other hand a solution of sodium carbonate was obtained, which, after evaporation and calcination, went into the trade as soda-ash. But this process was only applicable to the liquors obtained from the mechanical calcining-furnace (that is, with a minimum addition

of common salt); for in the liquors from the ordinary hand-worked furnaces there would be 1 part of NaCl to each 4 parts of  $\text{Na}_2\text{SO}_4$ , which would furnish a very weak soda-ash. This very ingenious process was worked out in all its details, and practically carried out on a very large scale, at the Bede metal-works; but it was abandoned, partly because the carbonic acid cost too much, and partly because no furnace-bottom could be constructed fit for resisting the acid liquors for any length of time; partly also because the quality of the soda-ash was too unequal; and finally because the copper was only obtained as sulphide, and had to be smelted at a greater expense than that precipitated by iron in the metallic state.

For this latter process either scrap wrought-iron, or scrap cast-metal, or "spongy iron" reduced from the residue is employed. Apart from the latter, the thinnest scrap is the best, such as the hoops of cotton or esparto bales; but as light scrap is generally somewhat dirtier than heavy scrap, the copper from the former is rather more impure than that from the latter. The precipitation takes place in wooden tanks exactly of the same kind as those used for lixiviation and furnished with a steam-pipe. They are filled with scrap-iron; copper-liquor is run upon it, and steam is turned on; the heating is continued till a bright strip of iron, held in the liquid, no longer indicates the presence of copper in solution. At Oker, according to the degree of concentration of the liquors, the boiling takes place twice or three times before all the copper is thrown down; the process lasts from one to three days, and requires as much iron as the weight of copper produced, which proves that a large portion of the latter must have been in solution as  $\text{Cu}_2\text{Cl}_2$ . Once a month the precipitated copper is removed from the tanks and washed.

After precipitation, at some works the liquor is passed through a hair sieve in order to separate the copper present in a fine state of division; the copper is washed off the residual iron by a jet of water, or a besom, etc., and left to settle in special tanks. At other works a less rough arrangement is in use, viz., round tubs with wooden agitators, an annular place being fenced off in their upper part for the scrap-iron. The agitation of the liquid causes every part of it to come into contact with the scrap-iron much more quickly, so that the



liquids are much sooner freed from copper than in the process first described; besides, the precipitated copper is at once washed off the iron and carried along with the exhausted liquor into settlers, and the process in the precipitating-tubs started again at once, after adding a little more iron.

A continuously acting apparatus for the precipitation of copper has been constructed by Hauch (*Dingl. polyt. J.*, ccxxiii. p. 286). It consists of a cask revolving round a horizontal axis, provided with ledges inside and filled with iron-borings; copper-liquor is let in, and is speedily exhausted by the rotation of the cask, the copper being at the same time washed off the iron. By combining several casks and systematically allowing the liquor to run into that cask which has been working the longest time, it is possible to obtain a continuous supply of fresh copper-liquor and a continuous running-off of exhausted liquor holding the copper in suspension. Another continuous copper-precipitating apparatus has been described by Kerpely (Wagner's *Jahresber.*, 1877, p. 165).

The precipitation takes place most quickly by employing "spongy iron," as is done at the Bede metal-works. This product is made by reducing ferric oxide at so low a temperature that the iron cannot combine with carbon and cannot melt, but remains in the finely divided state, as a "sponge." This method (which may possibly at some time play an important part in the metallurgy of iron and steel) was tried in England for the first time in 1837. Bronac and Deherrypon used it in 1859 for the precipitation of copper, but only in the dry way; but Gossage in the same year introduced the spongy iron in the wet method of copper-extraction. Further patents relating to this subject were taken out by Aas in 1861 and by Bischof in 1862.

Several furnaces have been proposed for this purpose, the best and most generally used being constructed as follows. It is a reverberatory furnace in which the flame, after having passed directly over the charge, returns below the furnace-bed, and thus heats the charge indirectly from below. Figs. 539 to 541 show all the essential details of the furnace. It is 28 ft. 9 in. long; the working bed has a length of 22 or 23 ft. with a width of 8 ft. Dwarf walls, *a a*, 9 in. high, divide it into three compartments, which, on one side have two

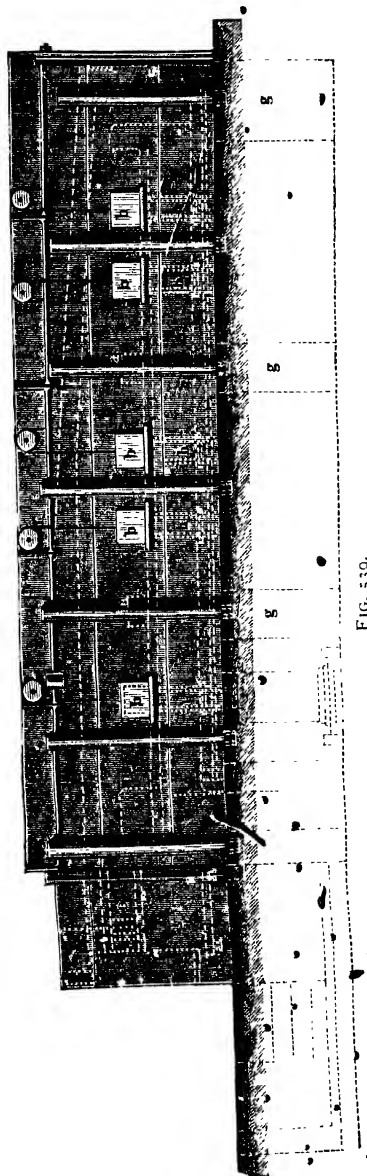


FIG. 539.

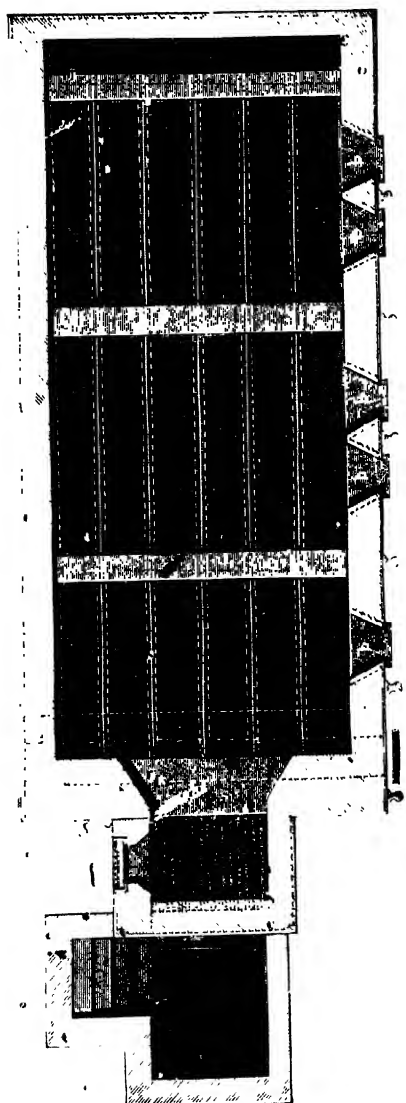


FIG. 540.

working-doors, *b b*, each. Each compartment is charged and finished by itself. The working-doors are of cast metal, and run air-tight in frames; the same is the case with the fire-door. The fireplace is constructed with a view of producing a reducing flame; the grate has a surface of  $4 \times 3$  ft.; and the bearers, *d*, are 3 ft., latterly even 4 ft.  $\frac{3}{4}$  in., below the fire-bridge; so that a very deep layer of fuel is obtained, which does not allow any oxygen to get inside the furnace. The furnace-bed is formed of fire-tiles 4 in. thick, with rabbeted edges, partly resting upon the walls forming the divisions of the lower

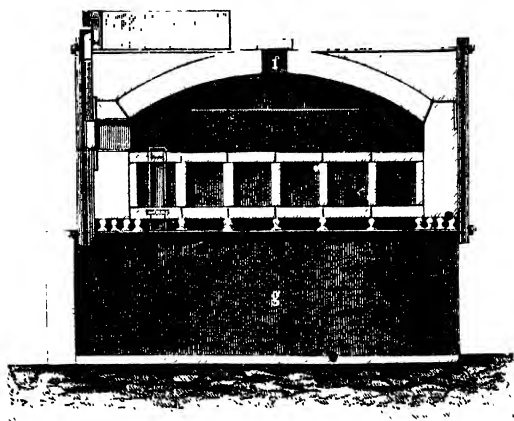


FIG. 541.

flues, partly upon railway-bars. The flame having travelled through these flues, descends in a vertical shaft along the fire-bridge, and thence goes to the chimney. In this descending shaft there is a fireclay damper, which is closed every time before a working-door or fire-door is opened. The 9-in. furnace-roof is surmounted by a flat cast-iron dish, *c*, supported by short pillars, for drying the ore and mixing it with coal; the mixture is charged into the furnace through the 6-in. pipes, *f*, carried through the arch. The whole furnace rests on brick pillars, *g*; and the floor on the working side must be so much higher than that on the discharging side that the discharging-boxes can be run underneath the furnace between the brick pillars. The discharging takes place through 6-in. pipes, *h*,

descending in front of the working-doors through the furnace-bottom and the lower flues.

The discharging-boxes (Figs. 542 and 543) are made of sheet-iron, of rectangular section, tapering towards the top. The cover, *a*, is fast, and has in its centre a 6-in. opening with upright flange, *b*, by which the box is connected with the discharging-tube. The bottom of the box is movable, and turns on one side on hinges, whilst the other side is fastened by bolts and cotters. The opening in the cover is easily closed by a metal plate. The whole is mounted on four wheels

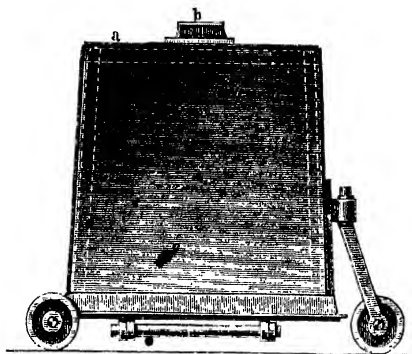


FIG. 542.

in such a way that they do not interfere with the movement of the bottom. Each box has a capacity of 12 cub. ft.

When the furnace is at a bright red-heat, it is ready for doing work. Every compartment receives a charge of 20 cwt. dry "purple ore" and 6 wt. coals, which have passed through a sieve with eight holes to the linear inch. As mentioned, the charging takes place from the cast-iron dish above the furnace-roof. The fire and working-doors are closed, so that the air enters exclusively through the coals on the grate, care being taken that the burning mass does not become hollow, lest uncombined oxygen should get inside the furnace. The time of reduction in the compartment nearest the fire-bridge varies from nine to twelve hours; in the second it is about eighteen hours, in the third about twenty-four hours. The depth of the charge lying

on the bed is about 6 in. During the time of reduction every compartment must be turned over twice, or even three times. Although during this time the damper is closed, a little air always enters the furnace; but the turning-over is indispensable, as the mass would otherwise cake together. The time above stated refers to a bright red-heat; a low, red-heat is sufficient for reduction; and the iron thus made is even better for the precipitation of copper; but as in this case much more time is required for reduction (up to sixty hours), this style of working does not pay. The fireplace being so deep, fresh coal need only

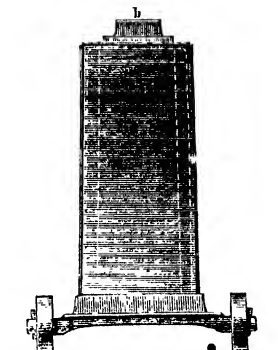


FIG. 543.

be thrown in twice or three times every twelve hours, say 15 cwt. for a ton of ore.

The completion of the reduction is ascertained by testing. A small sample is taken out, put on an iron plate, covered with a brick till it has become cold, and 1 g. of the (unoxidised) central part tested by a cupric sulphate solution of known strength, which is run from a burette on to the spongy iron, frequently stirring; from time to time a drop is put on a bright blade of iron, to see whether any stain of copper is produced upon it. When the reaction in any of the three compartments is finished, the damper is closed; two of the discharging-boxes are run underneath the furnace, and their mouths connected with the discharging-pipes by an iron hoop luted with clay; then the charge is raked down into the boxes as quickly as

possible. The boxes are then closed with their loose cover, run out again, and allowed to cool for forty-eight hours. They are then lifted by a crane and the cotters are knocked out; whereupon the bottom turns upon its hinges and the whole mass of spongy iron readily falls out, owing to the box tapering upwards. The sponge is then finely ground by a heavy edge-runner 6 ft. in diameter, and passed through a sieve with fifty holes per linear inch; it is now ready for the precipitation of copper.

Two different materials have been proposed for preparing spongy iron, viz., pyrites-cinders direct from the chemical works, and the "purple ore" of the copper-works themselves. The following analyses of average samples give a clear idea of the chemical difference between them:—

	Pyrites-cinders.	Purple ore.
	Per cent.	Per cent.
Ferric oxide . . . .	78.15	95.10
Iron . . . . .	3.76	..
Copper . . . . .	1.55	0.18
Sulphur . . . . .	3.62	0.07
Cupric oxide . . . .	2.70	...
Zinc oxide . . . . .	0.47	...
Lead oxide . . . . .	0.84	0.96
Calcium oxide . . . .	0.28	0.20
Sodium oxide . . . .	...	0.13
Sulphur trioxide . . .	5.80	0.78
Arsenic pentoxide . .	0.25	...
Siliceous residue . . .	1.85	2.13
	99.27	99.55

Both Bischof and Goossage proposed the direct use of burnt ore for preparing spongy iron, starting from the apparent advantage of utilizing its copper without the trouble of wet extraction. Unfortunately, however, the arsenic contained in the burnt ore remains in the spongy iron, gets into the copper, and greatly injures its quality. G. Bischof, indeed, in his patent of 1862, asserts that arsenic and lead volatilise; Gibb, however, admits this to be the case only for the lead to a great extent, whilst arsenic, being present mostly as arseniates of iron and copper, soon forms stable arseniurets. In fact the spongy iron made direct from pyrites-cinders contains nearly as much arsenic as was originally present in the cinders. On the other

and, the purple ore only retains faint traces of arsenic; it is therefore now exclusively used for the manufacture of spongy iron. The following is an analysis of the spongy iron made in the above way:—

	Per cent.
Ferric oxide . . . .	8.15
Ferrous oxide . . . .	2.40
Metallic iron . . . .	70.40
Copper . . . .	0.24
Lead . . . .	0.27
Carbon . . . .	7.60
Sulphur . . . .	1.07
Alumina . . . .	0.19
Zinc . . . .	0.30
Siliceous residue . . . .	9.00
	99.62

According to a later patent (B. P. 8093 of 1884), Bischof treats iron oxide with "water gas," obtained by passing steam over incandescent coke, after having removed any steam from it by cooling. The gas is strongly heated and is passed into the lower part of an inclined retort, into the upper end of which the ore is fed, and allowed gradually to descend to the lower part. Here it comes in contact with the mixed gases, and is reduced to the metallic state by the hydrogen contained in them. The spongy iron so obtained is discharged into a receptacle and cooled before exposure to the air. The remaining gases, deprived as they are of most of their hydrogen, are still combustible, owing to the CO present; they are met in the upper part of the retort by air and are burned, thus heating the iron oxide preliminary to its contact with hydrogen, and making external heating in most cases unnecessary. The operation is carried on at a low red-heat.

When spongy iron is employed for the precipitation of copper, continuous stirring is required, for which purpose at some works mechanical agitators are used, at others manual labour; at the Bede metal-works an india-rubber hose, through which a blast of air passes, is moved about in the tank. A Korting's blower would, no doubt, be the best apparatus for this purpose. Perfect mixture is thus obtained; and the precipitated copper only contains 1 per cent. metallic iron, with a great saving of space, apparatus, and labour, as against the work with scrap-iron. However, the greater cheapness of material and treatment in employing spongy iron is bought at the expense of



a greater contamination of the copper by unreduced iron oxides and carbon; at the majority of works, therefore, scrap-iron is still preferred. This, of course, depends also on the local price of the latter.

According to Bischof, when employing spongy iron the arsenic is only precipitated after a few hours, long after the copper has been precipitated, which thus remains free from arsenic. Gibb, however, from many years' experience on the large scale, states that he never found any trace of arsenic in solution after the copper had been precipitated, whichever form of iron or solution of copper might be employed.

*The composition of the copper precipitated by the various methods is shown by the following analyses (by Gibb):—*

	Precipitated by		
	Spongy iron.	Heavy scrap.	Light scrap.
	Per cent.	Per cent.	Per cent.
Copper . . . . .	67.50	7.250	67.50
Arsenic . . . . .	0.137	0.306	0.100
Silver . . . . .	0.011	0.046	0.066
Lead . . . . .	1.30	2.60	1.74
Ferric oxide . . . . .	5.15	4.41	7.56
Carbon . . . . .	5.10		
Silica . . . . .	3.20		

At Oker the composition of the copper precipitated by scrap-iron and dried at 100° C. was:—

	Per cent.
Cu . . . . .	77.45
Pb . . . . .	0.63
Ag . . . . .	0.10
Bi . . . . .	0.006
As . . . . .	0.04
Sb . . . . .	0.15
Fe <sub>2</sub> O <sub>3</sub> . . . . .	6.72
Al <sub>2</sub> O <sub>3</sub> . . . . .	0.99
Zn . . . . .	1.02
Mn . . . . .	0.02
Co + Ni . . . . .	0.03
CaO . . . . .	0.10
MgO + Alkalies . . . . .	2.71
SO <sub>3</sub> . . . . .	4.58
H <sub>2</sub> O . . . . .	1.19
Insoluble in acids . . . . .	0.61
Oxygen + moisture (by loss) . . . . .	3.654
	100.000

The following is an analysis of copper precipitated from pyrites-cinders at the Witkowitz works, dried at  $100^{\circ}$  (Schneider, *Fischer's Jahrbuch*, 1884, p. 163):—

	Per cent.	
Cu . . . . .	11.30	} together
Cu <sub>2</sub> O . . . . .	65.31	
Ag . . . . .	2.521	} 69.45 Cu
Au . . . . .	traces	
Bi <sub>2</sub> O <sub>3</sub> . . . . .	0.19	
Fe <sub>2</sub> O <sub>3</sub> . . . . .	3.86	
ZnO . . . . .	0.45	
As <sub>2</sub> O <sub>3</sub> . . . . .	1.18	
P <sub>2</sub> O <sub>5</sub> . . . . .	0.20	
CuCl . . . . .	0.32	
FeCl <sub>3</sub> . . . . .	0.16	
CoCl <sub>2</sub> . . . . .	0.29	
NiCl <sub>2</sub> . . . . .	0.07	
AsCl <sub>3</sub> . . . . .	1.32	
PbSO <sub>4</sub> . . . . .	2.19	
Na <sub>2</sub> SO <sub>4</sub> . . . . .	3.39	
CaSO <sub>4</sub> . . . . .	5.37	
MgSO <sub>4</sub> . . . . .	0.59	
H <sub>2</sub> O . . . . .	2.98	
	<hr/>	
	99.641	

This product is either sent to copper-smelting works or smelted at the wet-extraction works themselves. The copper precipitated from the *aqueous* solutions, if kept separate from that from the acid solutions, can always be smelted directly for blister-copper by adding to it lime and slags, but the copper from the *acid* solutions is frequently so impure that it has to be mixed with raw ore, or else with soda-waste and slags, and smelted for "coarse metal," which yields blister-copper only after a second roasting. Finally the usual refining takes place. At other works both precipitates are melted together, being charged at once into the furnace in the moist state. The slags produced in this operation, containing from 3 to 10 per cent of copper, are utilised by smelting them for coarse metal (in a circular blast-furnace, 3 ft. wide, with four tuyeres), with the addition of soda-waste (calcium sulphide and carbonate). The mass collects in a well, where the coarse metal separates from the slag, and the slag (a "singulosilicate") continually runs off

into a bogie. In order that such furnaces may be quickly taken down when the separated iron renders the smelting difficult or impossible, the upper furnace-shaft, together with its jacket, is supported on iron pillars, so that the proper smelting-shaft up to a height of 5 or 6 ft. stands quite free within the pillars. The coarse metal here obtained contains about 30 per cent. of copper, and is worked up in the usual way by calcining, smelting, and roasting.

The furnaces for smelting the copper precipitate used at English wet-extraction works are reverberatory furnaces of the well-known Swansea type. After smelting, the slag is skimmed off, and the copper tapped as blister. When spongy iron has been used, the excess of carbon prevents the copper from being melted directly to blister; therefore about one-half of the precipitate is calcined in large calciners similar to those for roasting burnt ores with salt. Here the carbon is burnt off and the copper partly oxidised; the calcined precipitate is mixed with raw precipitate and smelted, as above, for blister. The blister-copper is refined by roasting to oxidise the iron, sulphur, etc., followed by reducing by charcoal the oxide of copper produced in the roasting, and poling according to the method usually employed by the copper-smelter.

*Working-results of the Ordinary Copper-extracting Process.*—At the Duisburg Works (*cf.* Hasenclever, *Berl. Ber.*, 1896, p. 2862) the yield from 1000 kg. Rio-Tinto pyrites-cinders is 610 kg. purple ore, 34 kg. copper, 29.5 g. silver, and 0.1 g. gold. As the sale of the large quantities of purple ore is becoming difficult, the Duisburg Copper Company have started to work blast-furnaces of their own.

Clemmer (*Min. Ind.*, viii. p. 202) gives the following calculations of the cost of daily treating 200 tons of mixture of cinders and salts at Natrona:—Eighty workmen at wages from \$1.50 to \$2.50, together \$134.75; unloading cinders and salt, loading purple ore, \$35; 21 tons salt, \$63; pyrites fines, \$7; 20 tons coal, \$20; 5½ tons sheet-iron scrap, \$38.50; repairs, depreciation, management, \$40: total \$338.25, or \$1.87 per 2000 lbs. pyrites-cinders.

The copper produced is pure and tough. It takes a good place as a marketable article; and its composition in comparison with that of English copper made by the

ordinary method of smelting may be judged from the following analyses :—

	Copper from wet process.		"English" copper (Field's analyses).	
			B.S.	Tough.
	Per cent.	Per cent.	Per cent.	Per cent.
Silver . . . .	0.022	0.016	0.035	0.047
Arsenic . . . .	0.030	0.170	0.105	0.090
Antimony . . . .	...	trace	0.010	trace
Bismuth . . . .	0.006	0.019	0.035	0.130
Lead . . . .	...	0.002	...	...

The complete removal of the arsenic is said to be effected, according to Bischof (1862), by precipitation with spongy iron—according to Down (1870), by almost completely neutralising the copper-liquors with lime, followed by precipitation with scrap-iron; the foreign metals are said to remain in solution in this case (?). Gibb declares both statements to be entirely erroneous (*cf.* above, p. 1514); but it is quite possible that in Down's process the arsenic is removed at a previous stage, viz., on neutralising, as ferric arseniate.

*Extraction of the Silver contained in Burnt Pyrites.*—According to Phillips, the cupreous pyrites-cinders contain on the average 0.0027 per cent. silver and 0.0001 per cent. gold. These metals on calcining with salt are converted into chlorides; and, owing to the solubility of  $\text{AgCl}$  in  $\text{NaCl}$ , the silver is found mostly, the gold at least partly, in the liquors obtained by lixiviating the calcined ore. In order to further this, Phillips adds some more common salt in the lixiviating-tanks. These metals are now recovered in most works usually by the process of Claudet (B. P. 282 of 1870). This process consists in precipitating by a soluble iodide the silver from the liquors in the state of  $\text{AgI}$ , which is quite insoluble in solutions of chlorides. Only the first three liquors (which contain 95 per cent. of all the silver) are employed; the diluted state of the other liquors would make the recovery of the silver from them unprofitable. The liquors, before they undergo precipitation with iron, are completely settled, run into a gauged tank, and their contents of silver accurately estimated by adding to a certain volume hydrochloric acid and a solution of lead acetate, and

afterwards potassium iodide. The precipitate is collected on a filter, washed, dried, and fused with a flux of soda, borax, and the finest carbon. The lead regulus obtained is cupellated; and from the weight of the silver thus obtained, that contained in the liquors is computed. To the liquor a solution of potassium or zinc iodide of known strength is now added in sufficient quantity to precipitate all the silver; the iodide solution is diluted to such an extent that it amounts to about one-tenth the volume of the liquid; the precipitate is allowed to settle; the clear liquor is tested in the laboratory to see if all the silver is thrown down; and if so, it is run into the tanks for precipitating the copper, where it is treated in the usual way. The quantity of iodide employed for the precipitation is much larger than that corresponding to the silver present, since a portion of the lead is thrown down as  $PbI_2$ . Probably the silver is precipitated before the lead; but as it is not possible to bring all the silver contained in the liquor into contact with the iodide before the latter has also come into contact with molecules of lead, the precipitate always contains a good deal of lead; so that necessarily a corresponding excess of the precipitant is required.

The precipitate, consisting mainly of  $AgI$ ,  $PbI_2$ , and  $PbSO_4$  (which falls down on the cooling of the liquor), is well washed with water; and when a sufficient quantity of it has been collected, it is treated in the moist state and hot with metallic zinc and a little hydrochloric acid. Thus the  $AgI$  and  $PbI_2$  are decomposed completely, the  $PbSO_4$  partly, and a liquor containing *zinc iodide* is obtained, which is employed over again for precipitating argentiferous liquors in proportion to its percentage of iodine. On the other hand, a metallic sponge, mixed with pieces of zinc, is obtained having the following composition:—

	Per cent.
Ag . . . . .	5.95
Au . . . . .	0.06
Pb . . . . .	62.28
Cu . . . . .	0.60
ZnO . . . . .	15.46
$Fe_2O_3$ . . . . .	1.50
CaO . . . . .	1.16
$SO_2$ . . . . .	7.68
Insoluble residue . . . . .	1.75
Oxygen and loss . . . . .	3.62
	<hr/> 100.00

This is sent to the silver-works. Usually the argentiferous copper-liquor is first mixed with the solution of  $\text{ZnI}_2$  obtained in reducing the  $\text{AgI}$ , etc., and the last portion of the silver is precipitated by  $\text{KI}$ . A certain loss of the latter is unavoidable, whatever care be taken. In this way Phillips obtained about two-thirds of the total silver contained in the burnt ore, and about a similar proportion of the gold; several others have not been content with this, and have given up the process, probably because sometimes on calcining with salt too much  $\text{Cu}_2\text{Cl}_2$  is formed (its quantity varies from 0 upon 6.70  $\text{CuCl}_2$  to 0.62  $\text{CuCl}$  upon 3.75  $\text{CuCl}_2$ ), and in its presence the silver seems to be incompletely precipitated by iodides. At Phillips's works special care was taken to avoid the formation of cuprous chloride; and, perhaps on this account, Claudet's process has been more successful there than elsewhere.

An improvement on Claudet's process is asserted to be offered by the process of E. L. Mayer, patented in 1877. The copper-liquor is precipitated with a solution of glue and  $\text{KI}$ , whereby  $\text{AgI}$  is precipitated; the remaining solution contains very much copper and only a few thousandths per cent. of  $\text{Ag}$ . After the precipitate has settled down, a solution of tannin is added and a little more precipitate obtained. The precipitates are washed with similar dilute acid, as serves for dissolving the copper-ores in order to remove the copper they may contain. The acid is neutralised with lime, and treated with alkaline sulphides in a revolving drum till all iodine is removed; the solution containing iodides can be used for again precipitating silver. The remaining sulphides of lead, silver, etc., are to be worked for silver. The addition of glue and afterwards of tannin has for its object to conglomerate the extremely finely divided  $\text{AgI}$  (of which otherwise a portion would escape collection) into a larger mass.

Another process was worked out by Gibb and Gelstharpe (B. P. 624 of 1871). It is based on the observation, that if a copper solution containing very little silver is treated with sulphuretted hydrogen, by far the largest portion of the silver is thrown down as  $\text{Ag}_2\text{S}$  with the first portions of  $\text{CuS}$ . The  $\text{H}_2\text{S}$  is made from the tank-waste of alkali-works by treatment with dilute hydrochloric acid in wooden vessels; the hydrochloric acid enters the vessel underneath a false bottom made of boards

covered with furnace-slugs, and runs out near the top completely saturated. The vessels need not be air-tight, as the gas is aspirated from them by an air-pump, the delivery-pipe of which is provided with branches for every one of the precipitating-tanks; an india-rubber hose conveys the gas into these, and, when moved about in the liquid, sufficiently agitates it by the escaping gas. The process is continued until as nearly as possible 6 per cent. of the copper has been precipitated, which generally takes twenty minutes. The bulk of the copper, which otherwise shows on the average 18 oz. of silver per ton, shows after this treatment only 2 to 4 oz. The 6 per cent.  $\text{CuS}$  precipitated at first, however, contains 200 oz. silver per ton. The dilution of the gas by air seems to be favourable to the process. The precipitate is allowed to separate into clear liquor and denser mud; it is washed several times by decantation, and then pressed in a filter-press. The damp sulphides are calcined in an ordinary calciner; the product contains one-fourth of the copper as sulphate, the remainder as oxide or oxychloride, and the silver altogether as chloride. It is roughly ground, washed with water, and the solution of  $\text{CuSO}_4$ , which only contains 1 oz. of silver to the ton of copper, precipitated as usual. The residue, consisting mostly of  $\text{CuO}$ , is systematically extracted by hot concentrated solution of common salt, which dissolves nearly all the silver, leaving only 3 to 4 oz. of silver per ton of copper in the residue. The solution containing the silver is precipitated by milk of lime, the precipitate washed with water to remove the  $\text{CaCl}_2$ , then with dilute sulphuric acid to dissolve the copper, then again with water, and leaves at last a residue containing 9 per cent of silver as  $\text{AgCl}$ , worth £700 per ton. It contains beside principally the sulphates of calcium and lead. This treatment is stated to cost 9d. per ton of burnt ore, and to yield about 1 oz. of silver, of the value of 2s. 6d.; but, in this shape, it appears to have been discontinued.

Chadwick and Jardine (B. P. 2951 of 1875) described a new desilverising process, which was introduced at Henderson's works at Irvine. The copper liquors are diluted to 20° or 25° Tw., and a very weak solution of lead acetate is added, which is equivalent to the whole of the Ag, As, Sb, and Bi, less any Pb already contained in the pyrites. Usually about 230. g

of brown sugar of lead per ton are used. On agitating, a light yellow precipitate is obtained, consisting of 53 per cent. lead sulphate, 5 to 6 per cent. silver sulphate, and 3 oz. of gold per ton of precipitate (say, 0.01 per cent.). After thorough washing, the gold and silver can be obtained by smelting and refining in the usual way. The copper is said to be thus obtained free from As, Sb, and Bi.

According to Snelus (1875), finely divided iron dust is to be injected by a blower into the copper-liquors, just sufficient to precipitate 19 per cent. of all the copper; this is said to carry down 80 per cent. of all the silver contained in the solution.

Phillips (B. P. 3923 of 1887) prescribes mixing the copper precipitate with common salt and soda, moistening with water, and grinding in a pug-mill to a paste. The mass is dried and calcined in a reverberatory furnace, constantly stirring, till all the copper has been converted into CuO and all the silver into AgCl. The alkali added decomposes any volatile copper salt present, and almost entirely prevents any volatilisation of silver during the calcining-process. The AgCl is extracted from the calcined mass by treatment with a hot solution of common salt. (This is essentially like Augustin's process of 1840, applied to the extraction of silver from ordinary ores.)

Thilo (*Chem. Zeit.*, 1886, p. 822; *J. Soc. Chem. Ind.*, 1886, p. 584) gives special prescriptions for estimating the very small quantity of silver (0.003 to 0.008 per cent.) contained in pyrites cinders.

According to Clemmer (*Min. Ind.*, viii. p. 202, and ix. p. 289) the Claudet process (*supra*, p. 1517) has been entirely given up in the United States. The silver and gold are left in the cement copper, and are paid for at 95 per cent. of their value by the electrolytic refiners, as well as by the blue-vitriol works.

#### *Waste Liquors from the Copper Extraction.*

*Utilisation of the Sodium Sulphate contained in the Mother-liquors from the Precipitation of Copper.*—We have mentioned above the process of Gibb and Gelstharpe\* (p. 1519), which has been abandoned. At present the acid mother-liquors are everywhere allowed to run into the rivers, and the sodium sulphate



contained in them is lost. At a large copper-works for a time a process was employed by which ferric oxide was simultaneously obtained of great purity and fineness, so that it could be sold on the large scale for red paint. The acid liquors were boiled down to dryness in a brick furnace; the residual mass of sodium sulphate and chloride and iron salts was ignited, and ground very fine under edge-rollers; it was then carefully calcined in an ordinary calciner until all the iron salts were peroxidised. The mass was treated with hot water and allowed to settle; the ferric oxide deposited only required washing in order to become marketable as Venetian red. The solution (containing chiefly  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ) was concentrated in pans by means of steam circulating in a worm, an agitator preventing the salt from adhering in crusts to the bottom and sides of the pan and to the worm. At a concentration of 1.37 to 1.40 sp. gr. nearly all the sulphate was found to be separated; the liquor with the suspended salt was drained off the precipitate, which was washed with a little hot water and dried in a furnace. It contained only about  $\frac{1}{4}$  per cent. of  $\text{NaCl}$ , and not a trace of iron; so that it was very well adapted for glass-making. The high price of coals caused this process to be given up at the time, and it does not seem to have been taken up again. Probably the first step, viz., the evaporation of the acid liquors in a brick furnace, would present the same difficulties as in Gibb's process.

Ellis (*J. Soc. Chem. Ind.*, 1884, p. 613) proposed, in lieu of concentrating the liquors by heat, to do so only partially, and then to promote the crystallisation of sodium sulphate by cooling. He mentions no trial made on the large scale.

E. de Cuyper (*Ger. Ps.* 53261 and 54131) cools the liquor down to  $-3^\circ$ , at which temperature all the sulphate of soda crystallises out, whilst the chlorides of iron, zinc, sodium, etc., remain in solution even at  $-10^\circ \text{C}$ . After removing the Glauber's salts, the liquor is boiled down to dryness and the residue is calcined; pure ferric oxide is formed and is freed from the zinc chloride by lixiviation.

Jurisch (*Ger. P.* 41737) seeks to utilise the waste liquors after extracting the copper in the following manner:—They are almost neutralised, in tubs provided with mechanical agitators, by means of calcium carbonate; air and steam are blown

through, and in the same ratio as ferric sulphate is formed milk of lime is added, without, however, allowing all the acid to be saturated. When all the iron has been precipitated the mud is run into the settlers, the clear liquor is drawn off, and the deposit is passed through a filter-press. It contains some zinc salt, calcium sulphate, and carbonate, and can be made richer in iron by employing it the next time for the saturation of fresh liquor. The basic sulphate of iron thus formed can be employed for making sulphuric anhydride, oxide of iron, paint, etc. The liquor drawn off from it is mixed in an agitator with enough milk of lime to produce basic reaction; the zinc hydroxide precipitated contains some basic ferric sulphate, manganese, and calcium carbonate, and can be utilised in a suitable manner.

According to a communication of the inventor in the *Chem. Ind.*, 1888, p. 3, 50 cb.m. of waste liquor, containing 40 g.  $\text{ZnCl}_2$  per litre (from pyrites containing 1.5 to 3 per cent. Zn), would yield by his process 806 kg. ferric oxide mixed with calcium carbonate, 3600 kg. ammonium sulphate, 1444 kg. zinc oxide (50 per cent. Zn), 3245 kg. common salt, and a little potassium chloride. This statement is, however, only derived from analyses and laboratory trials, as Jurisch's process has not found any practical application. It will be interesting, though, to quote from his paper the composition of the liquor he worked with, obtained from the Witkowitz iron- and copper-works, with Hungarian pyrites.

One litre contained :—

	8.6 grammes free $\text{HCl}$ .
73.0	„ $\text{Na}_2\text{SO}_4$ .
3.6	„ $\text{K}_2\text{SO}_4$ .
16.9	„ $\text{NaCl}$ .
40.3	„ $\text{ZnCl}_2$ .
25.9	„ $\text{FeCl}_2$ .
3.1	„ $\text{FeCl}_3$ .
6.4	„ other matters.

He also gives a table of the copper and zinc percentages of a great many descriptions of pyrites.

Wigg, Steele, and Wigg (B. P. 13722 of 1884) mix the waste liquor with waste chloride-of-calcium liquor from the Weldon.

process in equivalent proportions, when a white bulky precipitate of calcium sulphate is formed, which is filter-pressed and sold as "pearl-hardening." The filtrate is treated with milk of lime, which precipitates ferrous hydrate, and this is oxidised by injection of air or chlorine, washed in a filter-press, and furnaceed to yield paint of various shades. Another patent of Wigg's (5620 of 1885) prescribes precipitating the iron by means of ammonium sulphide, and a third patent (11129 of 1885) describes apparatus for these treatments.

Bird's patent (B. P. 12458 of 1887) seems to contain no essential new feature.

Grabowski (Ger. P. 71917) concentrates the liquor by evaporation and crystallisation of Glauber's salt to sp. gr. 1.56; he then applies to them an electric current of great intensity, with lead and copper electrodes, by which arsenic and antimony are precipitated as metals at the cathode.

Brewer (B. P. 1348 of 1895) adds to the liquor a sufficient quantity of calcium-chloride solution, separates the resulting solution from the precipitated calcium sulphate (pearl-hardening), removes the silver, and afterwards the iron by calcium carbonate (in the shape of "caustic mud"), then nickel, cobalt, and manganese by bleaching-powder. This treatment practically leaves only the chlorides of zinc and calcium in the solution, which is electrolysed in order to obtain metallic zinc and free chlorine.

#### *Other Processes for extracting Copper from Pyrites-Cinders.*

In lieu of precipitating the copper by iron, Weldon (B. P. 5607 of 1882) proposed, as a cheaper process, to employ waste chloride of calcium from the Weldon process of manganese recovery, or other operations, which produces a mixed solution of copper and sodium chloride, holding calcium sulphate in suspension. The latter is to be separated by filtration, and the copper then precipitated by lime. This process does not seem to have found any practical application.

It is unnecessary to say that the copper can be precipitated from its solutions by the electric current, but we cannot enter into this subject in the present treatise.

Höpfner (Ger. P. 66096) adds to the copper-liquor so much  $\text{NaCl}$  or  $\text{CuSO}_4$  that the proportion  $\text{Na}_2\text{SO}_4 + \text{CuCl}_2$  is attained; then he adds metallic copper, whereby all the copper is precipitated as cuprous chloride, together with the silver in the metallic shape. From the mother-liquor, sulphate of soda is recoverable. Other modifications of the process are also proposed.

P. Spence (cf. *Alkali Inspector's Report*, 1877-78, p. 48) burns the pyrites (finely ground) in a furnace provided with mechanical stirrers that plough up the ore into ridges, making a change of surface every two and a half minutes (cf. pp. 488 *et seq.*). He asserts that in this way he burns 3 tons of ore in a furnace in a day, and renders all the copper soluble to 0.24 per cent.; thus he is able to wash out the copper salt and avoid the subsequent roasting with common salt. As much as 4.6 per cent. of sulphuric acid is left in the ore, rendering the copper soluble.

H. and Ch. H. Hills (B. P. 1621 of 1878) separate the coarse and fine portions of pyrites-cinders by sifting. The fine portions are calcined with salt in the usual manner; the coarse portions are lixiviated with dilute hydrochloric or sulphuric acid, and the copper is precipitated from the liquor by means of iron.

A very similar process of extracting copper from pyrites-cinders has been described by Jetzler (*Dingl. polyt. J.*, ccxvii. p. 478). He worked pyrites from Borsa-Bánya, in Hungary, containing only 1.01 Cu. The burnt ore decays easily on lying in the air; and after sifting off the not decayed ore through a sieve with ten meshes to 1 cm. square, the copper can be extracted by hot weak hydrochloric acid of 3° to 4° Tw.; probably ferric chloride acts here, chlorinating the lower sulphides of copper, and being reduced to  $\text{FeCl}_2$ . On washing, solutions of 24° Tw. are obtained, which, besides copper, contain Ag, Pb,  $\text{Al}_2(\text{SO}_4)_3$ , etc. The metals were precipitated by scrap-iron; and the precipitate was sold to a smelting-works according to its value of Cu and Ag. The process did not pay very well, as the residue could not be used as an iron-ore.

Another process was patented (in 1873) to Baron Leithner in Austria (*Dingl. polyt. J.*, ccxi. p. 349). The burnt ore (in this case containing about 1 per cent. of copper) is to be smelted with 36 per cent. calcium hydrate in a kiln heated by the waste gas of a blast-furnace; the product is to be smelted for pig-iron.

which now contains 2.09 per cent. Cu, and this is to be used for precipitating copper; so that its own copper is utilised as well.

Some British patents of Mason's (2984, 2992, and 2993 of 1877) seem to contain nothing new of any importance.

The whole of the processes connected with the wet extraction of copper, as far as published up to the end of 1878, and including many proposals or actually employed processes not mentioned here (because they do not refer specially to the treatment of pyrites-cinders from sulphuric-acid works), are described in a condensed form by Bode (*Dingl. polyt. J.*, ccxxxi. pp. 254, 357, 428).

The patents of Hargreaves and Robinson (B. Ps. 5601 of 1886 and 3704 of 1887) for extracting gold, silver, and copper from pyrites can be only briefly mentioned in this place.

Mr John Hargreaves informs me of the following results, obtained in 1887 by this process. He treats the pyrites-cinders, obtained in the usual manner, in a closed chamber with fire-gases and excess of air, in order to burn all the residual sulphur; the mass is allowed to cool down to the point where no cupric chloride can be volatilised, and is then treated with gaseous HCl till it is sufficiently decomposed. It is then lixiviated with water in tanks, after being moistened with strong hydrochloric acid; the residual ferric oxide is obtained in lumps, which are immediately ready for the blast-furnace.

The cinders originally employed contained, according to the size of the grain, from 1.02 to 1.09 per cent. Cu in a shape soluble in water, 0.71 to 1.09 soluble in hydrochloric acid, 1.61 to 2.79 insoluble. They were passed through a sieve with seven meshes per linear inch, and chlorinated as above described. The average from the upper part of the chamber then tested 3.90 per cent. Cu soluble in water, 0.63 soluble in weak hydrochloric acid, 0.56 insoluble; from the lower part of the chamber 3.51, 0.77, and 0.28 per cent. respectively. The treatment for burning the residual sulphur lasted from twenty-six to ninety-six hours, the chlorination from twenty-four to seventy-two hours. The liquors contained pretty much silver and a little gold; the washed residue contained only 0.8 to 0.12 per cent. copper. (I am not aware whether this process is now actually at work or not.)

Chase (Ger. P. 120277) mixes ground pyrites-cinders with a

little carbonaceous material, roasts the mixture at a full red-heat with access of air, mixes the product with a quantity of salt corresponding to the amount of copper present, and then continues the process in the ordinary way.

Pezzolato (Austr. P. 3882) mixes the cinders with 2 per cent. coal, and heats them with exclusion of air. The cooled and ground product is brought under the action of a magnetic ore-separator which takes out the iron compounds, together with the copper; from the acid solution the copper is precipitated by metallic iron, and ferrous sulphate is recovered from the solution left behind.

Tixier (Ger. P. 209508) extracts copper and other metals, except gold, from pyrites-cinders by treating them with chlorine *in statu nascendi* in an acid solution at  $70^{\circ}$  to  $80^{\circ}$ , e.g., by mixing them with 2 to 5 per cent. bleaching-powder or adding sulphuric acid or tepid hydrochloric acid.

*Treatment of Very Poor Cupreous Cinders.*—The case now occurs much more frequently than formerly, that ores containing only one or two per cent. of copper are burned. In such cases the cinders are too poor to apply the treatment described above, pp. 1472 *et seq.*, beginning with roasting the ground cinders with salt; on the other hand there is too much copper left in them to meet the demand of the iron-smelter. To overcome this difficulty the acid treatment, mentioned in some of the processes described, p. 1498, is applied. Frequently the cinders are previously exposed to the air for some time, in order to render some of the copper soluble in water; sometimes they are put in the leaching-vats quite fresh and warm. It depends upon the nature of the ore which of these two ways is preferable, and it must be found by experience in every practical case.

The acid treatment takes place in lead-lined wooden boxes, provided with a false bottom, and is carried on as described, pp. 1498 *et seq.*, beginning with weak liquor from a previous operation, to which is added a little sulphuric acid, 2 or 3 per cent. of the weight of the cinders. This acid liquor is left in contact with the cinders for two days; the strong liquor thus formed is then run off into the precipitating-tank and is replaced by weaker washings and ultimately by fresh water, so that the operation is finished in seven or eight days.

The weak washings formed are pumped back into other leaching-tanks by means of injectors. The copper is precipitated in lead-lined vats by means of scrap-iron, suspended in wicker baskets<sup>1</sup> or otherwise, at a temperature of 50° or 60° C. The precipitated copper mud is sold to iron-smelters, or is roasted into oxide in reverberatory furnaces and dissolved in hot weak sulphuric acid, to manufacture cupric sulphate.

By this treatment it is hardly possible to extract all the copper, but sufficiently so to render the cinders fit for the blast-furnace.

The manufacture of cupric sulphate from pyrites-cinders and low grade copper ores is described by Millberg in *Chem. Zeit.*, 1906, p. 511. The liquor obtained by lixiviation is treated with air, whereby the iron is precipitated in the shape of ferric oxide and the copper remains in solution as sulphate. If manganese is present, it is removed by precipitating the copper with milk of lime at a blasting-heat. Alumina is precipitated before the copper, and is thus kept out as well.

Mastbaum<sup>1</sup> in *Chem. Zeit.*, 1912, p. 30, reports a case where the shifting about of wet lixiviated pyrites-cinders in a steamer nearly caused it to founder.

#### *General Remark.*

*On laying out a copper-extraction works* the levels must be carefully attended to, so that the very large quantities of solid substances and liquors may be easily moved about. At Oker, Hebburn, etc., all the apparatus are arranged at different levels. The design of the Oker works has been published by Bräuning. (cf. the quotation on p. 1473). The top level is occupied by the charging-loft; to this the burnt ore and the salt are brought by bogies; attached to it are two edge-runners, each of which grinds daily 15 tons of ore and 2½ tons of salt down to a size of 2 mm. The mixture is taken by bogies to the furnaces, situated at a little lower level; the furnaces are heated by gas-producers, situated still lower down. Below the furnaces there follow, at three descending levels, the lixiviating-tanks, the precipitation-tanks, and cisterns for the "final liquor," from which it is pumped up again by injectors and used for lixiviating fresh ores.

*Statistical.*

According to the Report of the Chief Inspector of Mines for the year 1909, the quantity of cupriferous pyrites-cinders worked during that year in Great Britain was 414,680 tons, from which there was recovered 14,285 tons metallic copper, 1822 oz. gold, and 317,461 oz. of silver (the precious metals by Claudet's process, p. 1517).



## CHAPTER XIV

### APPLICATIONS OF SULPHURIC ACID AND STATISTICS

THE *principal applications* of sulphuric acid are the following :—

I. In a more or less *dilute* state (say from 144° Tw. downwards). For making sulphate of soda (salt-cake) and hydrochloric acid, and therefore ultimately for soda-ash, bleaching-powder, soap, glass, and innumerable other products. Further, for superphosphates and other artificial manures. These two applications probably consume nine-tenths of all the sulphuric acid produced. Further applications are :—for preparing sulphurous, nitric, phosphoric, hydrofluoric, boric, carbonic, chromic, oxalic, tartaric, citric, acetic, and stearic acids; for preparing phosphorus, iodine, bromine, the sulphates of potassium, ammonium, barium (*blanc fixe*), calcium (*pearl-hardening*); especially also for precipitating baryta or lime as sulphates for chemical processes; sulphates of magnesium, aluminium, iron, zinc, copper, mercury (as intermediate stage for calomel and corrosive sublimate); in the metallurgy of copper, cobalt, nickel, platinum, silver; for cleaning (pickling) sheet-iron to be tinned or galvanised; for cleaning copper, silver, etc.; for manufacturing potassium bichromate; for working galvanic cells, such as are used in telegraphy, in electroplating, etc.; for manufacturing ordinary ether and the composite ethers; for making or purifying many organic colouring-matters, especially in the oxidising mixture of potassium bichromate and sulphuric acid; for parchment paper; for purifying many mineral oils, and sometimes coal-gas; for manufacturing starch, syrup, and sugar; for the saccharification of corn; for neutralising the alkaline reaction of fermenting liquors, such as molasses; for effervescent drinks; for preparing tallow previously to melting it; for recovering the fatty acids from soap-suds; for destroying vegetable fibres in mixed fabrics; generally, in dyeing, calico-printing, tanning;

as a chemical reagent in innumerable cases ; in medicine against lead-poisoning, and in many other cases.

II. *In a Concentrated State*.—For manufacturing the fatty acids by distillation ; purifying colza oil ; for purifying benzene, petroleum, paraffin oil, and other mineral oils ; for drying air, especially for laboratory purposes, but also for drying gases for manufacturing processes (for this, weaker acid also, of  $140^{\circ}$  Tw., can be used) ; for the production of ice by the rapid evaporation of water in a vacuum ; for refining gold and silver, desilvering copper, etc. ; for making organo-sulphonic acids ; manufacturing indigo ; preparing many nitro-compounds and nitric ethers, especially in manufacturing nitro-glycerine, pyroxyline, nitro-benzene, picric acid, and so forth.

III. *As Nordhausen Fuming Oil of Vitriol (Anhydride)*.—For manufacturing certain organo-sulphonic acids (in the manufacture of alizarine, eosine, indigo, etc.) ; for purifying ozokerite ; for making shoe-blackening ; for bringing ordinary concentrated acid up to the highest strength as required in the manufacture of pyroxyline, and other purposes.

#### *Statistics on Sulphuric Acid.*

Concerning former periods we refer to the data given in former editions of this book, which we do not repeat here, especially as they are partly based on assumptions and cannot lay claim to any accuracy. We confine our data to such as are obtainable for more recent periods.

*Great Britain and Ireland*.—The number of sulphuric-acid works under Government inspection in England and Ireland in the year 1889 amounted to 221, including those in which the acid was entirely used up at the works themselves for alkali, manure-making, etc. In Scotland this number was 32. In 1899 the figures were: 175 works in England and Ireland, 24 in Scotland ; in 1901, 172 works in England and Ireland, 24 in Scotland. Only two of these worked the contact-process. In 1907 there were 154 ; in 1908, 162 ; in 1910, 150 sulphuric-acid lead-chamber works in Great Britain, apart from 90 factories working by other processes, or merely concentrating and distilling the acid.

There are no statistics on the production of sulphuric acid in the United Kingdom. In our last edition a calculation is made for it from the pyrites imported, which is not an accurate basis

for it, and which we do not repeat now. We may take it as an approach to the truth that the production of sulphuric acid in the United Kingdom, calculated as real  $\text{H}_2\text{SO}_4$ , has been about a million tons per annum, more or less, for a number of years past.

From the Official Annual Statement on the Trade of the United Kingdom with Foreign Countries and British Possessions (edition of 1911), we take the following figures on the exports and imports of sulphuric acid (evidently including fuming O.V.) from and into Great Britain during the last years. The figures denote hundredweights:—

In 1911, 6150 tons were imported and 9630 tons exported.

	1906.	1907.	1908.	1909.	1910.
Sulphuric acid imported (nearly all from Belgium and also from Germany) . . . . .	89,904	75,086	68,545	74,246	99,759
Exported acid made in United Kingdom . . . . .	97,812	77,770	100,847	144,864	133,063
Exported acid made abroad . . . . .	4	2,392	81	17	...
British-made acid exported to foreign countries . . . . .	10,422	6,282	18,318	50,231	21,423
British-made acid exported to British possessions . . . . .	87,390	71,488	82,169	94,633	111,631
Foreign-made acid exported . . . . .	4	2,392	81	17	...

*Germany.*—Here also we abstain from giving statistical data for former years and refer to our last edition; all the more as we had to point out already at that time that the data obtainable were of little value. The case is different with the estimates made by Hasenclever for the year 1882; but this is too remote now, and we confine ourselves to more recent years.

Hasenclever (*Chem. Ind.*, 1899, p. 25) quotes the German production in 1898 as follows:—

	Acid of 142° Tw. Tons.
Made from 55,483 tons German pyrites . . . . .	80,515
„ 332,004 „ foreign pyrites . . . . .	571,046
„ zinc-blende . . . . .	136,868
Made at Freiberg, Oker, and Mansfeld from mixed ores . . . . .	50,738
Made from gas-oxide . . . . .	6,915

845,582 = 659,554 tons  
real  $\text{H}_2\text{SO}_4$

This is estimated on the basis of a yield of 143 parts acid 142° Tw. on 100 parts German pyrites, or 172 on 100 Spanish pyrites.

In 1900 the importation of sulphuric acid into Germany was 20,634 tons, the exportation 37,738 tons. In 1902, 22,205 tons were imported, 477,666 tons exported.

The quantity of *fuming* sulphuric acid produced in Germany is stated = 4685 tons in 1897; 14,092 tons in 1898; 19,526 tons in 1899; but this seems to include only that acid which came into the market, not that used up in the factories themselves for the manufacture of tar-colours, etc.

Since, in 1901, 488,632 tons pyrites were imported into Germany, or 156,000 more than in 1898, we may, on the assumption that the other raw materials did not undergo an essential change, estimate the quantity of real  $H_2SO_4$  made in Germany in 1901 = 878,002 tons. This equals the production of the United States in that year, and nearly approaches that of the United Kingdom.

In 1904 the exportation of sulphuric acid from Germany was 52,696 tons, the importation 16,087 tons. The total production in that year, according to Hasenclever (*Chem. Ind.*, 1905, p. 52), was:

	Tons.	
From pyrites . . . . .	8,100,000	sulphuric acid 60° Bé.
„ blende and spent oxide of gas-		
works . . . . .	200,000	„ „
	<hr/>	
	1,300,000	

Of this quantity about 500,000 or 600,000 tons was used for the manufacture of superphosphate, 150,000 tons for ammonium sulphate. About 250,000 tons was obtained by the contact-process in the form of high-strength acid and used in the manufacture of dyes and of explosives. The remainder was used in the manufacture of saltcake, of aluminium sulphate, and for other purposes.

	Tons.		Tons.	
In 1907 Germany imported	59,753	and exported	49,902	sulphuric acid.
„ 1909	74,384	„	63,817	„
„ 1910	86,743	„	60,581	„
„ 1911	99,653	„	64,888	„

Accurate official statistics concerning the manufacture of sulphuric acid,  $SO_3$  and  $SO_2$  in 1908, are found in *Chem. Ind.*, 1910.

p. 753. The total production of sulphuric acid in Germany in that year was 1,150,524 tons, calculated as  $\text{H}_2\text{SO}_4$ , of which only 6 per cent. was more than 100 per cent. acid, *i.e.*, containing or consisting of anhydride. This proves that the chamber-process still prevailed by far over the contact-process. The number of men employed was 6883. Of the raw materials, 55.8 per cent. was pyrites (of which only 11.4 per cent. of German origin, the remainder mostly Spanish) and 35.5 per cent. blende (of which 81.3 per cent. of German origin); 78.9 per cent. of the sulphuric acid obtained was made from pyrites, 15.7 per cent. from blende, the remainder from lead matte, gas-oxides, S and  $\text{H}_2\text{S}$ . The production of liquid  $\text{SO}_2$  was 5430 tons. The amount of pyrites-cinders obtained was 489,311 tons (of this 60.3 per cent. cupreous cinders, 30.2 ordinary, 9.5 containing much zinc); the weight of roasted blende was 357,202 tons. In the year 1909 Germany produced 1,296,316 tons ordinary O.V. and 138,395 tons Nordhausen O.V.

For 1910 Duisberg (*Z. angew. Chem.*, 1912, p. 6) estimates the production in Germany at  $1\frac{1}{4}$  million tons  $\text{H}_2\text{SO}_4$ , 300,000 tons of which were made in the two largest factories for coal-tar dyes.

According to *Chem. Ind.*, 1912, p. 503, Germany produced sulphuric acid (calculated in tons of  $\text{H}_2\text{SO}_4$ ):—

Year.	Total.	From pyrites.	From zinc-blende.	From other materials.
1909	1,223,075	970,120	193,944	59,011
1910	1,380,739	1,093,722	217,630	69,378

There existed the following number of sulphuric-acid works:—

Year.	Chamber plants.	Contact plants.	Mixed plants.	Consuming pyrites, tons.	Zinc-blende, tons.
1909	103	80	5	738,437	458,402
1910	103	79	6	835,878	458,464

*France.*—According to *Chem. Ind.*, 1911, p. 416, the consumption of pyrites in that country and the amount of sulphuric acid manufactured, as calculated from the former on the bases

of 45 tons pyrites = 100 tons sulphuric acid, has been as follows:—

Year.	Pyrites consumed.	Sulphuric acid manufactured.	Year.	Pyrites consumed.	Sulphuric acid manufactured.
	Tons.	Tons.		Tons.	Tons.
1900	397,000	883,000	1905	518,000	1,150,000
1901	461,000	1,024,000	1906	589,000	1,308,000
1902	423,000	940,000	1907	615,000	1,366,000
1903	408,000	907,000	1908	592,000	1,317,000
1904	426,000	947,000	1909	508,000	1,130,000

According to *L'Engrais*, 17th November 1911, *Chem. Ind.*, 1912, p. 78, France in 1911 manufactured 1,350,000 tons sulphuric acid 52° to 53° B $\acute{e}$ . in 73 acid works mostly from pyrites; only 30,000 tons were made from zinc-blende and only 2 works burnt brimstones. The factories are distributed as follows:—

Locality.	Number of Factories.	Production of acid.
		Tons.
Paris and neighbourhood . . . . .	10	200,000
North of France . . . . .	11	300,000
North-west . . . . .	9	130,000
East . . . . .	2	10,000
Central . . . . .	9	250,000
West . . . . .	13	200,000
South-west . . . . .	7	130,000
South . . . . .	12	130,000
Total (France) . . . . .	73	1,350,000

Most of the factories worked the old lead-chamber process; but the Société St Gobain partly by the contact-process of the Badische, and the Malétra and Kuhlmann companies by the Grillo-Schröder process.

*Austria* in 1902 imported 12,460 tons sulphuric acid, and exported 9451 tons. In 1902, 4 works had introduced the contact-process. The total amount of sulphuric acid manufactured was about 200,000 tons, strength not mentioned (*Z. angew. Chem.*, 1903, p. 215). In Hungary, in 1909, there were 9 works, producing 240,000 tons O.V. per annum.

*Belgium* in 1899 produced 210,000 tons acid of 60° Bé. = 164,000 tons  $\text{H}_2\text{SO}_4$ . About 60 per cent. of this was made from blende, 40 per cent. from pyrites. In the year 1903 the production was 310,000 tons of 60° Bé.

*Italy* in 1879 possessed 10 sulphuric-acid works, most of them of small size, producing 7140 tons of acid of 106°, 2210 tons of 172°, and 2520 tons of 168° Tw.; say, altogether, 9883 tons  $\text{H}_2\text{SO}_4$ . Since that time the production of sulphuric acid has very largely increased. In 1895 Candiani (*Chem. Ind.*, 1895, p. 153) stated the total chamber-space of the Italian factories = 108,000 cb.m., which, if they were fully at work, would be equal to a production of at least 65,000 tons  $\text{H}_2\text{SO}_4$  per annum. A statement by Chiaraviglio, "from official sources," according to which Italy, in 1900, produced 220,000 tons acid, calculated as  $\text{H}_2\text{SO}_4$ , seems very doubtful.

According to *Z. angew. Chem.*, 1903, p. 117, there was produced in Italy:—

	In 1900.	In 1901.
	Tons.	Tons
Sulphuric acid (strength not stated) . . . . .	229,555	235,172
Sulphur dioxide (liquid) . . . . .	1.4	13.5
Nitric acid . . . . .	2,071	2,069

According to *Chem. Ind.*, 1912, p. 146, Italy produced in the year 1910, 844,643 tons sulphuric acid, value 22,956,000 lire.

*Russia* produced, according to official information (*Chem. Ind.*, 1900, p. 542), in 1899 about 100,000 tons sulphuric acid from 50,000 tons pyrites (about 12,000 tons of which was mined in Russia) and 16,500 tons sulphur. Great part of this was made at Baku for the chemical treatment of petroleum products. The importation of sulphuric acid from other countries was but slight: about 500 tons in 1894; 280 tons in 1895; 220 tons in 1896; 165 tons in 1897. The import duty for ordinary sulphuric acid is 22 kopeks (gold) per pud = about £2, 3s. per ton; for fuming acid or anhydride = 1 rubel (gold) per pud = £9, 18s. per ton. The selling-price varies from 0.75 to 1.00 rubel per pud for strong acid, about 0.60 rubel for chamber-acid, 0.40 rubel for "black acid" (recovered from the acid-tar of petroleum).

refineries by diluting with water, removing the tar, and concentrating the aqueous portion by evaporation).

According to *Chem. Zeit.*, 1901, p. 313, formerly all sulphuric acid in Russia was made from Sicilian sulphur, of which, even in 1898, 16,000 tons was imported. Now the pyrites found in the Ural Mountains, containing up to 7 per cent. copper, has largely come into use. Of this, 16,000 tons is obtained per annum, and another 33,000 tons is imported from Scandinavia and Spain. In 1908 Russia produced 160,000 tons ordinary and 4600 tons fuming O.V.

Fedetijew (*Z. angew. Chem.*, 1902, p. 865) estimates the Russian consumption of Sicilian sulphur at 20,000 tons per annum, of Russian pyrites at 30,000 tons; in 1901 73,600 tons pyrites were imported from Spain, Portugal, Sweden, and Norway. The amount of acid produced was about = 125,000 tons  $H_2SO_4$ , and about 1000 tons 30 per cent. fuming acid. The factories are situated at Wiatka, Kasan, Baku, St. Petersburg, Riga, Moskow.

Suler (*Vern. V. Intern. Kong. f. angew. Chem.*, 1905, i. p. 747) makes the following statements on the annual production of sulphuric acid in Russia, the unit being acid of  $54^\circ$  Bé. =  $120^\circ$  Tw.:—By the Ushkoff works, 20,000 tons; by the Tentelew works, 24,000 tons; in 25 other works, 112,000 tons. There was hardly any importation from abroad. The raw material was formerly mostly Sicilian sulphur, nowadays pyrites, which is partly got in Russia (Ural, Caucasus, Donetz), but mostly imported from Spain, Portugal, Sweden, and Norway. Most of the sulphuric acid is consumed in the Baku district for purifying crude petroleum and lubricating oils.

According to *Chem. Trade J.*, 1911, xlvii. p. 230, the Russian Imperial Society says that the production of sulphuric acid during the last ten years has not been very satisfactory, and depends more and more on foreign raw material, notwithstanding the wealth of pyrites in Russia. During that period the importation of raw material for sulphuric acid rose threefold; and the home production fell considerably. Sulphuric acid is imported in increasing quantities, though not a great deal. There are in Russia 60 to 65 sulphuric-acid works, including those where it is only a by-product (petroleum <sup>6</sup>



refineries, colour works, gunpowder works, etc.). The annual production is about 200,000 tons.

In 1908 (*Chem. Zeit.*, 1909, p. 765) Russia produced 163,800 tons ordinary and 4500 tons fuming sulphuric acid, corresponding to an increase of 66 per cent. within the last ten years.

For the *United States* we possess unusually good materials for statistics in a report made by the Washington Census Bureau (United States Census Bulletin, No. 210). In the original the quantities are quoted in pounds weight and the costs in dollars per short ton (of 2000 lbs.). I reduce them in the following to *long* tons (of 2240 lbs.) both for quantities and costs; and I also give the equivalent of the quantities in real monohydrate ( $\text{H}_2\text{SO}_4$ ).

In the year 1890 there were 105 establishments making sulphuric acid, which produced

Acid of 50° Bé.	Value per ton.	Acid of 60° Bé.	Value per ton.	Acid of 66° Bé.	Value per ton.
Tons.	Dols.	Tons.	Dols.	Tons.	Dols.
450,832	7.62	9098	10.77	158,274	16.37
equivalent in $\text{H}_2\text{SO}_4$ :					
= 279,515		6186		144,612	

Grand total = 430,313 tons  $\text{H}_2\text{SO}_4$ ; value, 7,679,473 dols.

In the year 1900 there were 127 establishments (with only 28 chemists!), which produced

Acid of 50° Bé.	Value per ton.	Acid of 60° Bé.	Value per ton.	Acid of 66° Bé.	Value per ton.
Tons.	Dols.	Tons.	Dols.	Tons.	Dols.
875,392	7.46	15,635	12.92	336,856	14.29
equivalent in $\text{H}_2\text{SO}_4$ :					
= 542,743		10,632		309,907	

Grand total = 863,282 tons  $\text{H}_2\text{SO}_4$ ; value, 14,247,185 dols.

[This does not seem to include the acid made from zinc-blende and other smelting-operations, which, according to *Eng. and Min. J.*, August, 1902, p. 182, in 1900 amounted to 75,650 long tons of 66° Bé.]

Of the 127 works reporting in 1900, 31 burnt brimstone only, 79 pyrites only, 17 both brimstone and pyrites. (Nothing is said about blende.) The report abstracted here gives as the average production of 20 works a production of 402 lbs. acid of

50° Bé. [say, 62 per cent.  $\text{H}_2\text{SO}_4$ ] from 100 lbs. brimstone, with a consumption of 4.29 lbs. nitre, and 234 to 160 lbs. (average 204) acid of 50° Bé. from 100 lbs. pyrites, with a consumption of 1.2 to 2.5 lbs. of nitre per 100 lbs. pyrites. [The yields here quoted, mechanical averages from very discrepant sources, possess of course very little practical value. The statistics given by Gilchrist in *J. Soc. Chem. Ind.*, 1899, p. 460, are rendered obsolete by the above official report.]

In the *Transactions of the 5th International Congress of Applied Chemistry*, 1905, p. 770, Falding gives a list of sulphuric acid chamber-plants completed or in course of construction in the United States since 1900. He enumerates 37 firms, with a chamber capacity of altogether 6,537,000 cub. ft.; also a number of contact-plants by the Schröder-Grillo, the Mannheim, the Frasch, and the Badische system. Further statistics are found in *Z. angew. Chem.*, 1906, p. 1944.

Munroe, in Bulletin 92 of the United States Census Bureau, gives the following figures for the production of sulphuric acid in the United States:—

	1890.	1900.	1905.
	Tons (short).	Tons (short).	Tons (short).
Total $\text{H}_2\text{SO}_4$ reduced to 50° Bé. . . . .	783,569	1,548,123	1,869,437
50° Bé. . . . .	504,932	953,439	1,169,141
60° Bé. . . . .	10,190	17,012	48,688
66° Bé. . . . .	177,267	382,279	411,165
Oleum . . . . .	..	...	13,268
Nitric acid . . . . .	...	63,085	708,380

One hundred and fourteen establishments in 1905 burned pyrites only, 19 brimstone only, 10 both, and 6 used roaster-gas from zinc and copper smelters.

In the year 1909, according to *Z. angew. Chem.*, 1910, p. 1922, the production of sulphuric acid in the United States was about equal to that of Germany, but there were still 23 states and territories without any factories of that kind. The Duckton Sulphuric Copper and Iron Company in Tennessee is able to furnish 200 tons of acid of 60° Bé. *per diem* (*Chem. Zeit.*, 1910, p. 827).

According to the United States Census Bureau Report

(quoted in *J. Soc. Chem. Ind.*, 1911, p. 1449) the total production of sulphuric acid in the United States, reduced to 50° Bé., has been as follows (quoted in "short tons" of 2000 lbs. each):—

1904 : 1,869,446 tons, of which 467,514 tons as chief product  
 1909 : 2,797,723 " " 933,848 " "

The remainder being made in establishments engaged primarily in the manufacture of other products, or consumed in establishments where manufactured. The number of factories for sulphuric, nitric, and mixed acids in 1909 was 42, and a capital of \$18,726,000 was invested in them.

For 1910 Duisberg (*loc. cit.*) estimates the production in the United States at 1,200,000 tons  $H_2SO_4$ ; another estimate (in *Z. angew. Chem.*, 1911, p. 642) gives 2 million tons of 60° Bé. = 1,560,000 tons  $H_2SO_4$ . For 1911 Phalen, in *Chem. Trade J.*, 1912, i. p. 651, gives the production of the United States reduced to 50° Bé. = 2,688,466 short tons, exclusive of acids of greater strength than 66° Bé.

Wedge (*Proc. Eighth Ins. Cong. Appl. Chem.*, 1912, pp. 271 *et seq.*; *J. Soc. Chem. Ind.*, 1912, p. 874) makes the following statements on the production of sulphuric acid in the United States, reckoned as at 50° B., in the year 1911:—

	Tons.
For the manufacture of phosphate fertilisers . . .	2,400,000
For refining petroleum products . . .	300,000
For use in the iron and steel and coke industry . . .	200,000
For the manufacture of nitrocellulose, cellulose, nitro-glycerine, etc. . . . .	150,000
For other purposes . . . . .	200,000
	<hr/> 3,250,000

Of this acid was made:

	Tons.
From pyrites . . . . .	2,665,000
From copper sulphide ores smelted in blast furnaces . . .	275,000
From zinc sulphide ores . . . . .	285,000
From brimstone . . . . .	25,000

About 10 per cent. of the total production of acid is made by contact-processes, especially for the manufacture of nitro-cellulose and similar products. The practice of nodulising cinder from pyrites burners for use as iron ore has become general in all localities where there is a market for it.

Japan in 1900 consumed about 28,000 tons sulphuric acid 50° Bé., mostly from native pyrites. Nearly 10,000 tons of this were consumed by bleaching-powder works, 8500 tons petroleum by refiners; over 1000 tons were exported, partly to China (*J. Soc. Chem. Ind.*, 1900, p. 299). This statement contrasts very much with that given below.

In *Chem. Zeit.*, 1902, p. 1231, we find a report on the manufacture of sulphuric acid in Japan by Professor T. Nishigawa, of which we give a short abstract. The first works was erected in 1872 for the Imperial Mint at Osaka by an Englishman, Mr Kinder, in the old-fashioned style of burning brimstone on plates without towers. These were followed by similar works in 1880. In 1883 Nishigawa erected the first factory on modern principles, and many others followed, principally at Osaka and Tokio. Several of these have reached a daily make of 80,000 to 100,000 lbs. acid of 50° Bé. They are built on thoroughly modern principles, with Gay-Lussac and Glover towers, partly also with Lunge towers. Since 1895 brimstone has been partly replaced by pyrites. Except the first, all of them have been constructed by Japanese chemists, and they are all managed by Japanese. There were then 9 acid-works, producing nearly 50,000 tons pure  $H_2SO_4$  per annum.

According to *Chem. Ind.*, 1910, p. 420, Japan in 1907 produced 102,210 tons O.V.

The total production of sulphuric acid in the world in 1906 is estimated by "La Nature" (quoted in *Z. angew. Chem.*, 1907, p. 164) at 4.1 million tons. Of this 1.1 million tons was made in Great Britain; 900,000 tons in Germany; 850,000 in the United States; 500,000 in France; 200,000 in Italy; 200,000 in Austria-Hungary; 165,000 in Belgium; 125,000 in Russia; 50,000 in Japan.

[This estimate is of very doubtful value!]

For 1910 Duisberg (*loc. cit.*) estimates the world's production of sulphuric acid at 5 million tons, calculated as  $H_2SO_4$ .



## ADDENDA

p. 14. *Volatility of Sulphur*.—F. Jones (*Proc. Manchester Lit. and Phil. Soc.*, 1911, p. 14; *J. Soc. Chem. Ind.*, 1912, p. 815) states that sulphur volatilises very perceptibly on boiling with water, or on heating to 100° in a dry current of air, hydrogen sulphide and thiosulphuric acid being always formed at the same time.

p. 15. *Blue Sulphur* has been further studied by J. Hoffmann (*Z. Chem. Ind. Kolloide*, x. p. 275; *Abstr. Amer. Chem. Soc.*, 1912, p. 3235).

pp. 20 and 21. *Statistics of the Production and Exportation of Sicilian Sulphur*.—For the year 1911, the German Consulate at Palermo reports a production of 391,908 tons and an exportation of 396,996 tons.

According to *Mineral Industry of the United States*, the exportation of sulphur from Sicily in the year 1911 to various countries was as follows :—

	Tons.
United States and Canada . . . .	8,560
France . . . . .	105,300
Italy (mainland) . . . . .	75,400
Germany . . . . .	28,660
Norway, Sweden, Denmark . . . .	30,200
Greece and Turkey . . . . .	25,300
Great Britain . . . . .	19,800
Russia . . . . .	23,485
Austria and Hungary . . . . .	35,700
Holland . . . . .	12,650
Portugal and Spain . . . . .	22,550
Belgium . . . . .	10,300
Other countries . . . . .	58,325
Total . . . . .	456,230

The total production of sulphur in *Italy* in 1911 was 456,200 tons.

p. 23. *Production of Sulphur in Germany* in 1911, 46,054 tons.

p. 25. *Sulphur in New Zealand*.—According to the report of the Government Trade Commissioner (*Chem. Trade J.*, ii. p. 300) in 1912, a company, with a capital of £100,000, has purchased White Island, in the Bay of Plenty, with the object of working the sulphur deposits there. It is said that there are 40 acres of rock sulphur ore containing about 84 per cent. of pure sulphur, as well as hot sulphur springs which pour out thick streams of molten sulphur containing about 94 per cent. of pure sulphur. The company propose to make borings to reach the source of these springs.

p. 25. *Production of Sulphur in Japan*.—In 1909, 36,000 tons; in 1910, 43,155 tons (of which 17,400 tons was shipped to the United States).

In *Persia*, sulphur is found at Khamir (between Bender Abbas and Lingah), at Schiraz, and on the Demavend mountain, north-west of Hindianina.

p. 27. *Sulphur in the United States*.—The following statements are taken from the report of the U.S. Geological Survey, through *Chem. Ind.*, 1913, p. 9:—

	1909.	1910.	1911.
Sulphur produced in the States, long tons . . .	239,312	255,534	265,664
" crude, imported into the States, long tons (mostly from Sicily) . . .	26,914	28,647	24,250
" " flowers of sulphur . . .	...	...	3,891
" " refined sulphur . . .	...	...	985
" exported from the States, long tons . . .	37,142	30,742	28,103

Price of brimstone, per long ton (New York) . . .	\$22
" roll sulphur, per 100 lbs. . . .	\$1.85 to 2.15
" flowers of sulphur, per 100 lbs. . . .	\$2 " 2.40
" sublimed sulphur, per 100 lbs. . . .	\$2.20 " 2.60

p. 28. *Sulphur in Peru*.—According to *Mineral Industry*, 1912, p. 681, in the Département Piura, 150 tons of sulphur were reported to be produced *per diem*, but according to the same source this is probably an exaggeration.

p. 29. *World's Production of Sulphur.*—In *Mineral Industry*, 1912, p. 682, the following quantities of sulphur are reported to have been obtained by the respective government organs. The figures denote metric tons. They do not comprise the sulphur recovered from alkali-waste, which in Great Britain amounts to between 20,000 and 30,000 tons.

	1906.	1907.	1908.	1909.	1910.	1911.
Austria-Hungary	15,358	24,199	17,429	12,856	15,976	...
Chili . . .	4,598	2,900	2,705	4,508	...	...
France . . .	2,713	2,000	2,189	2,900	2,641	...
Germany . . .	178	176	811	1,185	1,272	1,251
Greece . . .	1,000	1,000	1,000	1,000	1,000	...
Italy . . .	499,814	426,972	455,312	435,660	430,360	414,671
Japan . . .	27,589	33,329	33,419	36,319	43,155	...
Spain . . .	700	3,612	13,872	21,750	30,133	...
United States	298,704	312,731	312,700	303,000	259,699	246,300
Total	845,956	801,911	829,437	817,608	...	...

p. 33. *The Frasch Process for the Production of Sulphur.*—According to the U.S. Geological Survey Report, most of the sulphur in the United States is now produced in Louisiana by the Union Sulphur Company according to the Frasch process. For superheating the water there are 130 boilers of 150 to 300 h.-p. each, in sets of 15 to 20 boilers, all heated with oil, of which each set requires 700 barrels *per diem*; the total annual consumption is about 7,000,000 barrels. The daily consumption of water is about 7,000,000 gallons. Each well produces sometimes 400 to 500 tons sulphur *per diem*; the total average yearly production is over 250,000 tons.

According to Vail (*Eng. and Min. J.*, 1912, xxiv. p. 449), a plant for the recovery of sulphur by a process similar to the Frasch process is to be erected in Texas by the Freeport Sulphur Company; the possible production of sulphur from the native rock in that place is estimated at 120,000 tons per annum.

p. 41. *Sulphur from Pyrites.*—L. P. Wright (B. P. 26128 of 1911) heats pyrites by means of an electric retort-furnace to a very high temperature, thereby most of the sulphur is set



free and is collected in the distillate; the residue consists of iron containing some sulphur, and may be refined in known manner.

p. 42. *Production of Sulphur from Sulphur Dioxide.*—Teed, Sulman, and Picard (B. P. 14628 of 1911) mix gases containing  $\text{SO}_2$  with reducing-gases, like producer-gas or water-gas, and carry the mixture over a heated contact-mass consisting of magnesia, or calcium sulphate, or ferric oxide, e.g., magnesia bricks heated to a red heat, which produces the reactions:  $\text{SO}_2 + 2\text{CO} = 2\text{CO}_2 + \text{S}$ , and  $\text{SO}_2 + 2\text{H}_2 = 2\text{H}_2\text{O} + \text{S}$ .

In Young's "thiogen process" (as reported by F. L. Wilson, *Chem. Zeit. Rep.*, 1912, p. 514)  $\text{SO}_2$  is reduced to S by carbon, employed in the form of atomised mineral oils, with the assistance of ferric oxide or calcium sulphide, containing iron, as catalyser, after having previously removed any free oxygen. An experimental plant has been erected at Campo Seco in California.

p. 44. *Production of Sulphur from Hydrogen Sulphide.*—Fritzsche (B. P. 25454 of 1911) treats  $\text{SO}_2$  and  $\text{H}_2\text{S}$  simultaneously, or in succession, at a temperature of  $60^\circ$  to  $70^\circ$  with a liquid in which aluminium hydroxide or basic aluminium sulphide is suspended. Soluble acid sulphites are formed, which with  $\text{H}_2\text{S}$  give a precipitate of sulphur and basic sulphate, which latter is regenerated to acid sulphite by means of  $\text{SO}_2$ .

p. 46. *Reducing Sulphur to Fine Powder.*—Fabre (Fr. P. 437015) adds to ground sulphur, intended for agricultural or industrial purposes, a little animal gall, previously moistened with alcohol, which causes it to be easily moistened.

p. 48. *Chancel's Sulphurimeter.*—Frésehüus and Beck especially recommend the sulphurimeter sold by Joh. Greiner of Munich, which deviates in its dimensions from the instruments supplied by French firms. These instruments have been officially adopted by the Swiss Union of Analytical Chemists, which has also issued special prescriptions for the sulphur to be used for vineyards (*Z. anal. Chem.*, xlv., p. 760).

p. 50. *Flowers of Sulphur*.—A. R. Scott and A. Meyer (Fr. P. 439258) prevent the formation of crystallised or solid sulphur upon the floor of the chamber by subjecting the sulphur vapours, before being admitted to the condensing chamber, to a vigorous atomisation by a suitable apparatus.

p. 51, line 12, read "Dantony" for "Dantong."

p. 53. *Estimation of Sulphur in Spent Oxide of Gas-works*.—Refer here to the processes of Zulkowsky, and of Dennstedt and Hassler, *infra*, pp. 101 *et seq.* Pfeiffer (*J. Gasbeleucht.*, xlviii. p. 977) describes a similar process; another process is described in the same journal, liv. p. 837.

p. 53. *Estimation of the Impurities of Sulphur*.—Ceruti (*Boll. chim. farm.*, xliii. p. 421) estimates the impurities by treating the sulphur with aniline at 120° to 130°, which extracts the S and leaves the impurities behind.

Fresenius and Beck (*Z. anal. Chem.*, xlii. pp. 31 *et seq.*) drive off the sulphur by heating a little over 200°, weighing the residue, burning it and weighing the ashes, the difference between these two weighings representing organic impurities.

p. 64. *Formation of Pyrites Beds*.—A paper on this has been published by Doss (*Chem. Zeit.*, 1912, p. 540).

p. 69. *Pyrites in Germany*.—Production in 1911: 217,439 tons; importation, 862,000 tons (of this, 753,000 tons from Spain).

p. 75. *Pyrites in Sweden*.—Production in 1911: 21,592 tons.

p. 84. *Pyrites in the United States*.

			Tons.
Production in the year	1911	.	299,594
Importation	"	1909	688,843
"	"	1910	803,851
"	"	1911	1,006,310
Consumption	"	1909	902,385
"	"	1910	1,030,290
"	"	1911	1,262,540

p. 87. *Production of Pyrites (in tons).*

	1909. <sup>1</sup>	1910. <sup>1</sup>	1911. <sup>2</sup>
Belgium . . . . .	214	213	...
Bosnia . . . . .	(?)	571	...
Canada . . . . .	57,718	48,871	32,000
France . . . . .	268,918	250,432	240,000
Germany . . . . .	195,060	215,708	217,000
Austria-Hungary . . . . .	97,412	92,464	100,000
Japan . . . . .	27,066	78,418	9,000
Italy . . . . .	130,152	165,688	170,000
Norway . . . . .	278,352	322,000	350,000
Portugal . . . . .	194,861	176,300	477,000
Russia . . . . .	(?)	50,000	...
Spain . . . . .	254,853	294,184	3,605,000 <sup>3</sup>
Sweden . . . . .	15,850	25,445	...
Great Britain . . . . .	8,429	10,393	150,000(?)
United States . . . . .	247,070	227,280	300,000
Turkey . . . . .	...	...	100,000

<sup>1</sup> According to *United States Mineral Industries*.<sup>2</sup> According to Wetzig (*Z. angew. Chem.*, 1912, p. 2418).<sup>3</sup> Includes cuprififerous pyrites.

Wetzig (*loc. cit.*) states the *consumption of pyrites* in Germany for other purposes than the manufacture of sulphuric acid = 150,000 tons, principally for the manufacture of cellulose. The Norwegian cellulose makers consume about 40,000 tons pyrites. In the United States about 1,000,000 tons pyrites are consumed for the manufacture of sulphuric acid, 300,000 tons for other purposes.

Wetzig also gives the following figures, denoting thousands of tons:—

*Importation of Pyrites.*

	1908.	1909.	1910.	1911.
Germany . . . . .	659	691	792	862
United States . . . . .	668	588	807	1001
England . . . . .	780	791	812	892
France . . . . .	347	350	380	450
Austria . . . . .	130	141	153	150
Italy . . . . .	164	150	115	115
Belgium and Holland . . . . .	145	145	180	250
Russia . . . . .	100	100	115	115
Denmark, Sweden, Portugal . . . . .	(?)	24	30	34
Australia, Africa . . . . .	(?)	14	28	36
Total . . . . .	2993	3094	3412	3995

*Exportation of Pyrites (thousands of tons).*

	1908.	1909.	1910.	1911.
Spain . . .	2491	2416	2588	3107
Portugal . . .	364	295	322	293
Norway . . .	217	216	306	315
Canada . . .	60	57	80	100
Turkey . . .	78	80	100	150
Servia . . .	...	21	36	32
Total . . .	3210	3085	3432	3997

*Consumption of Pyrites (thousands of tons).*

	1906.	1907.	1908.	1909.	1910.	1911.
<i>Germany—</i>						
Own product . . .	196	196	219	197	215	217
Imported . . .	579	742	659	691	792	862
Total . . .	775	938	878	888	1007	1079
<i>United States—</i>						
Own product . . .	261	247	223	247	238	300
Imported . . .	597	582	668	688	807	1001
Total . . .	858	829	891	935	1045	1301
<i>Great Britain—</i>						
Own product . . .	9	9	9	8	9	9
Imported . . .	759	769	780	791	812	892
Total . . .	768	778	789	799	821	901
<i>France—</i>						
Own product . . .	265	282	240	240	240	240
Imported . . .	321	330	367	350	380	480
Total . . .	586	612	587	590	620	690
<i>Italy—</i>						
Own product . . .	122	126	131	149	170	170
Imported . . .	(?)	116	164	150	115	115
Total . . .	...	242	295	299	285	285
<i>Austria—</i>						
Own product . . .	112	99	95	98	100	100
Imported . . .	(?)	130	130	141	153	150
Total . . .	...	229	225	239	253	250

p. 94. *Dry Methods for decomposing Pyrites.*—Warunis (*Z. anal. Chem.*, l. p. 270) estimates the sulphur in pyrites by fusing it with sodium carbonate and cupric oxide.

p. 100. *Analysis of Pyrites.*—Smoot (*Eng. and Min. J.*, 1912, p. 412; *J. Soc. Chem. Ind.*, 1912, p. 918) removes the heavy metals from the aqua regia solution of pyrites, before precipitating the sulphuric acid by barium chloride, by means of electrolysis. Of the pounded sample 0.5 g. (or 0.6868 g. for convenience of calculation) is weighed off and treated in a 250 c.c. beaker with a mixture of 3 parts of nitric acid (sp. gr. 1.42) and 1 part of hydrochloric acid (sp. gr. 1.20), to which four or five drops of bromine have been added. The covered beaker is allowed to stand at the ordinary temperature for half an hour, then heated in a steam- or water-bath till action has ceased, then the cover is removed and the liquor evaporated to dryness. Then 5 c.c. of hydrochloric acid are added, the cover is replaced till effervescence has ceased, and then removed, rinsed, and the evaporation to dryness repeated. The residue is treated with 25 c.c. of hot water and rinsed into the electrolytic cell, consisting of a conical lipped beaker of about 150 c.c. capacity, with a tubulure near the bottom for the platinum wire leading into the mercury cathode. The liquid is made up to about 75 c.c., a flat platinum spiral is introduced as anode, an inverted funnel is made to rest on the wall of the beaker above the liquid, and a current of 0.8 to 1 ampère is passed for five or six hours (or a weaker current overnight). The funnel and the beaker sides are now washed down, the liquid decanted into a 300 c.c. beaker as closely as possible, and the beaker and mercury are washed with four successive quantities of 25 c.c. of water. The mercury is then poured out of the side away from the lip, and the empty beaker, especially the lip, is rinsed clean. The liquid is now filtered from the 300 c.c. beaker into an 800 c.c. beaker, the filter washed, the liquid diluted to 450 c.c. (660 c.c. if 0.6808 g. has been used), heated to boiling, and whilst boiling 25 c.c. (34 c.c. of 10 per cent. solution of barium chloride added slowly. The author uses for this a "precipitation pipette," consisting of a large thistle-funnel, with the stem bent so as to pass under the cover-glass of the lip of the beaker, whilst the funnel is supported by a

wire-stand on the cover-glass. The end of the stem is so drawn out that 25 c.c. of liquid will be delivered in five minutes. The precipitate is filtered and washed as usual, and the filter burnt off with the precipitate. The error due to the excess of occluded barium chloride over the solubility of barium sulphate amounts to from 0.01 to 0.04 per cent. A number of determinations gave results averaging 0.18 per cent. higher than those obtained with the Lunge method. Lead to the extent of 0.04 g. to 0.5 g. does not interfere with the accuracy of the results.

Allen and Bishop (*J. Soc. Chem. Ind.*, 1912, p. 919) oxidise a sample of the ore by means of a solution of bromine in carbon tetrachloride, followed by nitric acid; then follows the reduction of the iron by aluminium powder, and the cold precipitation of the barium sulphate in a large volume of the liquid by the slow addition of a dilute solution of barium chloride. It is stated that the results of this process are generally 0.1 to 0.15 per cent. higher than those obtained by the usual methods.

Shumacher (*Scient. Amer.*, 1912, p. 179) describes a "quick method." He brings 0.5 of the finely powdered pyrites (or pyrrhotite) in a porcelain dish into contact with 10 c.c. aqua regia, allows to stand for fifteen minutes and evaporates to dryness. After cooling, 90 to 100 c.c. of 5 per cent. hydrochloric acid are added, and solution, after having turned dark green, is transferred quantitatively into a 250-flask. Here the iron is precipitated by 6 c.c. of liquor ammoniæ; the liquid is filled up to the mark and well mixed up. One hundred c.c. of it are filtered into beaker, 2 c.c. concentrated hydrochloric acid are added, heated to boiling, and 10 c.c. of a 10 per cent. solution of barium chloride added, whereupon the precipitated barium sulphate is treated in the usual manner.

The reporter on this process in *Chem. Zeit. Rep.*, 1912, p. 350, remarks that it is very questionable whether by this "quick method" a complete decomposition of the pyrites is effected, and losses of sulphuric acid by the ferric hydrate precipitate are avoided. I for my part entirely agree with these remarks.

The volumetric estimation of combined sulphuric acid by means of benzidine, first proposed by Vaubel (*Z. anal. Chem.*, 1896, p. 821) has been applied by many chemists in various

modifications, of which we here only mention those proposed by Raschig (*Z. angew. Chem.*, 1903, pp. 617 and 818; 1906, p. 332), and by Friedheim and Nydegger (*ibid.*, 1907, p. 19).

p. 109. *Estimation of Arsenic in Pyrites*.—Schürmann and Böttcher (*Chem. Zeit.*, 1913, p. 49) discuss the former methods for estimating arsenic in pyrites and describe in detail their own method, which is founded on decomposing the pyrites by a mixture of sulphuric and chromic acid, reducing the arsenic to arsenious acid by  $\text{SO}_2$  or  $\text{Cu}_2\text{Cl}_2$ , precipitating it by  $\text{H}_2\text{S}$  and estimating the As in the  $\text{As}_2\text{S}_3$  either volumetrically by Mohr's method, or gravimetrically by oxidation and precipitation as argentic arseniate.

p. 117. *Sulphuric Acid from Sulphide Ores*.—According to the *Bull. U.S. Geol. Surv. for 1911*, in the year 1911, 400,000 tons of various sulphide ores were roasted at Ducktown, Tenn., in seven large blast furnaces, and thereby daily 160 tons, exceptionally 200 tons, sulphuric acid of 60 B $\acute{e}$ . was obtained.

The Amer. P. of J. Parke Channing, No. 962498 (Ger. P. 253492) protects a special treatment in the "pyritic smelting" of sulphide ores, by which gases for working up in lead-chambers are obtained. He adds in the smelting 1 per cent. carbon for every 4 per cent. of "available" sulphur, and works with so much air, that there is 4 or 5 per cent. oxygen present in the gases over and above that which is required for the formation of sulphur trioxide.

p. 120. *Manufacture of Sulphuric Acid from Spent Oxide of Gas-works*.—Messel (*J. Soc. Chem. Ind.*, 1912, p. 856) states that so far he had not been successful in working with the spent oxide of gas-works (referring to the catalytic process). It has the advantage of relative freedom from arsenic, but the drawback of producing an acid which is not so bright and colourless as that made from pyrites. The colour is due to the organic matter in the raw material, and to the formation of nitric oxide from its nitrogenous constituents.

p. 129. *Statistics on Nitrate of Soda*.—In 1911 the production in Chili was 54,804,856 quintales (1 quintal = 46 kg.).

the exportation 53,250,327 quintales (of which 40,062,507 went to Europe). The total production for 1912 was estimated at 58,000,000 quintales.

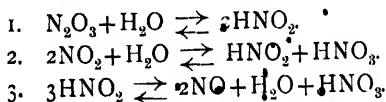
p. 151. *Error*.—On line 11 from the bottom read: 1903 in lieu of 1905.

p. 160. *Manufacture of Nitric Acid*.—F. W. de Jahn (Amer. P. 1023138, transferred to the General Chemical Company) agitates sodium nitrate with sulphuric acid under diminished atmospheric pressure at a temperature below the fusing-point of the bisulphate formed, preferably below 384° F. (195° C.).

p. 168. *Manufacture of Nitric Acid Free from Lower Oxides*.—Moore and Hall (B. P. 28892 of 1910) avoid the absorption of lower nitrogen oxides in the condensation of nitric acid by passing the vapours upwards between cooled tubes, in such manner that the liquid formed on running down over these tubes gets sufficiently heated for avoiding the absorption of the lower oxides. Further intimate contact of the liquid with the hot vapours is attained in a chamber, provided with partitions and filled with pumice, etc.

p. 178. *Manufacture of Nitric Acid*.—F. W. de Jahn and the General Chemical Company (Ger. P. 252374; Amer. P. 1023133) effect the decomposition of nitrates by sulphuric acid under diminished pressure at lower temperatures, and in a short time by constantly agitating the mass, and avoiding the fusion of the bisulphate formed. The best temperature is 135°, and in the end the vacuum is brought to 28 ins.

p. 184. *Obtaining Nitric Acid Free from the Lower Nitrogen Oxides*.—Brüffer and Derand (*Comptes rend.*, clv. p. 582) have studied the conditions of the formation of nitric and nitrous acid from nitrogen oxides and water by employing the law of the action of masses at wide limits of pressure and temperature. They established reversible equilibria as follows:—





p. 194. *Concentration of Nitric Acid*.—Imray (B. P. 15948 of 1911) dissolves in ordinary nitric acid of 60 to 62 per cent. gaseous or liquid nitrogen peroxide, and treats the mixture with oxygen, whereby the peroxide is oxidised into nitric acid and concentrated nitric acid is obtained. The same process is described in the Ger. P. 249328 of the Salpetersäure-Industrie-Gesellschaft.

The Farbwerke Höchst, whose Fr. P. 432990 is mentioned in the text, obtained for the same process the B. P. 15948 of 1911; Ger. P. 249328 and Austr. P. appl. 7082. According to their Ger. P. 249329 the oxygen is employed in the compressed state, and the escaping oxygen and nitric oxide gases are re-introduced into the process.

Schlarb (Ger. P. 243840) obtained concentrated nitric acid from any description of nitrous gases by treating them with water in the presence of the oxides or basic nitrates of iron, aluminium, or chromium, driving off the nitric acid from the nitrate liquors obtained (if necessary, after concentrating them in vacuo) by heating, continually under diminished pressure. Thus marketable nitric acid of 40° Bé. and more, as clear as water, is obtained; the basic nitrates or hydroxides remaining behind are used over again for the absorbing process.

p. 195. *100 per cent. Nitric Acid*.—Friderich (B. P. 319 of 1911) treats a molecular mixture of liquid nitrogen peroxide and water with oxygen. According to his B. P. 493 of 1911, in lieu of liquid nitrogen peroxide the product of absorbing  $N_2O_4$  by wood, charcoal, etc., may be used.

*Preparation of Pure Nitric Oxide*.—The Farbwerke Höchst (Fr. P. 428657) prepare NO from nitric acid of not more than 40° Bé. by electrolysing it, applying graphite or platinum cathodes.

*Preparation of Pure Nitrogen Peroxide*.—The Badische Anilin- und Sodafabrik (Ger. P. 231805) remove from nitric oxide or gaseous mixtures free from oxygen, containing NO, any  $NO_2$  present, dry the remaining NO, and convert it into  $NO_2$  by means of dry oxygen or air.

According to their Ger. P. 242288 nitrogen peroxide is recovered from gaseous mixtures containing a small quantity of it, in a solid form by the cooling consequent on compressing.

the gases, removing the heat produced by the compression, and allowing the gases to expand adiabatically.

p. 199. *Recovery of Nitric Acid from Waste Nitrating-mixtures with Sulphuric Acid.*—According to Pohl (*Z. angew. Chem.*, 1912, p. 1853) the Deutsche Ton- und Steinzeugwerke at Charlottenburg denitrate these mixtures in columns made of quartz-glass ("vitreosil"), 250 mm. (9.8 ins.) wide and 2290 mm. (9 ft. 6 in.) high, in which, when heated by steam of 200°, 8 tons of waste mixtures (containing 5 per cent. nitric acid) can be treated in twenty-four hours. Each column consists of three pipes of 760 mm. (2 ft. 6 in.) width each, fitted with quartz rings resting on a perforated plate. The superheated steam is introduced in the centre of the bottom pipe by a tube of such shape that the steam blows straight upwards. The nitric-acid vapours issue from the top of the tower into an air-cooled condenser, consisting of five vitreosil turills of 2.65 cub. ft. capacity, with vertical tubes; the vapours not condensed there go into a wash-tower filled with pieces of quartz.

The recovery of strong sulphuric acid from such waste nitrating mixtures will be described in Chapter IX.

p. 201. *Manufacture of Nitric Acid.*—Frank and the Siemens & Halske Company (Ger. P. 246613) bring nitrogen oxides in the presence of oxygen or air into contact with the salts of halogen acids, with complete exclusion of moisture, in fixed or revolving chambers, with or without agitating-gear, or in various other ways described in the specification. In this way, e.g., it is possible to convert potassium chloride into 80-per-cent. nitrate.

p. 206. *Manufacture of Nitric Acid from Atmospheric Nitrogen by High Temperatures.*—According to "Stahl und Eisen," 1912, pp. 1571 *et seq.*, the process of Häusser, described in the text, has been carried out by the Deutsche Stickstoffindustrie A. G. at an experimental factory. They employ a gas of the ordinary composition of coke-oven gases, viz., 44 per cent. hydrogen, 26 per cent. methane, 14 per cent. carbon monoxide, 1 per cent. other hydrocarbons, 3 per cent. carbon dioxide, 1 per cent. nitrogen, 8 per cent. oxygen. The air serving for combustion is heated and mixed with oxygen. The explosion

takes place in a steel shell of 100 litres capacity, with a cooling-jacket. The products of the combustion pass through a cooler for separating the water, then through an oxidising-tower, and the remainder into the outer air. Details are given on the effect of working with various proportions of oxygen and at various temperatures and pressures. It is expected that with an initial pressure of 6 atm., addition of 33 per cent. oxygen, and pre-heating the air to 250° to 330°, the yield of nitric acid per cubic metre of the gas can be raised to 200 g. According to the *Journ. Gasbeleucht.*, 1912, p. 1037, this process will be carried out on a large scale at the coke-ovens at Hayingen. In *Z. Verein. deutsch. Ingen.*, 1912, p. 1157, Häusser describes some recent improvements of his process.

p. 208. *Oxidation of Atmospheric Nitrogen*.—Lecesne (Fr. P. 437397) employs red (ferruginous) bauxite for fixing atmospheric nitrogen, after converting the bauxite by means of hydrogen sulphide into a porous, black mass which takes up nitrogen from the atmospheric air in the shape of nitrates or nitrides. If, according to his Fr. P. 424514, the bauxite is employed in the shape of powder, amides are formed.

Coutagne (Fr. P. 437504) heats a mixture of carbon with the oxides of Si, Ca, Ba, Mg, Al, B, Ti, etc., in an electric furnace, and slowly passes nitrogen through the mass under high pressure, whereby the nitrides of those metals are formed.

The Compagnie Bordelaise de Produits Chimiques (Fr. P. 440218) oxidises atmospheric nitrogen by passing air over the oxides of Co, Mn, Cr, Ni, Ba, Pb or Ce at temperatures over 500°, and at once cooling the gases by blowing in cold, compressed air.

Askerösy and Rényi (*Z. Elektrochem.*, 1913, p. 23) discuss the observation made upwards of a hundred years ago, that on heating native peroxide of manganese in a current of air (or CO<sub>2</sub>) minimal quantities of nitrogen oxides are produced; these most likely are not formed from atmospheric nitrogen, but are present in the manganese ore in a hitherto unknown form.

p. 213. *Investigations of the Electrolytic Formation of Nitric Acid*.—Such investigations have been made by Lowry (*J. Chem.*

Soc., cl. p. 1152 of 1912); Tausent (*Z. Elektrochem.*, xviii. p. 314); Russ (*Oesterr. Chem. Zeit.*, 1912, p. 316).

Franz Fischer and Emil Hene (*Berl. Ber.*, 1912, pp. 3652 *et seq.*) investigated the formation of nitric oxide in the high-tension arc flame. They drew from their work the following conclusions:—

1. The formation of NO in the high-tension arc is preceded by an activation of the oxygen, not of the nitrogen.

2. The highest yield of NO is obtained if sparked oxygen acts on unsparked nitrogen; almost twice as much as when air is sparked and then allowed to mix with more air. The lowest yield takes place if sparked nitrogen is blown on pure oxygen.

3. Much more NO is obtained if the air coming out of the high-tension arc flows into oxygen, than if it is mixed with air or nitrogen and then cooled.

4. Probably in actual practice much better yields of NO will be obtained if air is not passed through the high-tension arc, but oxygen, employing magnetite electrodes, and if it is afterwards quickly mixed with nitrogen and cooled down. The air would be first fractionated by the Linde process, the oxygen obtained would be exposed to the high-tension arc, and subsequently mixed with the nitrogen.

p. 214. *Technical Processes for the Electrolytic Manufacture of Nitrogen Oxides and Nitric Acid.*—Ellis (Amer. P. 1007683); Russ and Ehrlich (Fr. P. 463620); The Swedish Nitric Syndicate (Ger. P. 233031); Lowry (*Proc. Chem. Soc.*, 1912, p. 64); C. F. R. von Koch (B. P. 14523 of 1911).

p. 224. Russ (*Z. angew. Chem.*, 1912, p. 586) continued the investigations of Haber and König.

p. 232. *Electrolytic Manufacture of Nitric Acid from Air by Pauling's Process.*—A further patent of the Salpetersäure-Industrie-Gesellschaft, Gelsenkirchen (Ger. P. 250968) describes a furnace for the purpose.

According to *Chem. Ind.*, 1912, p. 650, the Southern Electrochemical Company is going to erect a factory for employing that process at Nitrolee, near Great Falls, N.C., which is to

work with 20,000 h.-p. and to produce 16,000 tons nitrate of lime per annum.

p. 236. *Birkeland and Eyde's Process for the Electrolytic Manufacture of Nitric Acid from Air*.—According to E. K. Scott (*J. Soc. Chem. Ind.*, 1912, p. 586), a special kind of stoneware packing in lieu of quartz for the condensing-towers has effected a saving of 50 per cent. in space.

The further development of this process was described by Eyde in September 1912 at the International Congress of Chemists at New York (*J. Indust. and Engin. Chem.*, 1912, pp. 771 *et seq.*). The factory at Notodden now works with 60,000 h.-p., those at Notodden, Svaelfos, Lienfos, and Rjukan altogether with 200,000 h.-p. and 1340 workmen.

p. 246. *Processes of the Badische Anilin- und Sodafabrik for the Electrolytic Production of Nitric Acid from Air*.—For producing light-arcs further patents have been obtained:—Ger. Ps. 232926, 233729, 233967, 237562, 237796, 238367, 238368, 238958; B. Ps. 22715 of 1909; 13097 of 1910.

For absorbing the nitrogen oxides: Amer. P. 1039325 (by Schönherr and Brode); 1029528 (by Bosch, Keller, and the Badische Anilin- und Sodafabrik).

p. 247. *Nitrogen Oxides formed by the Combustion of Nitrogen*.—Papers on the estimation of these oxides have been published by Lunge and Berl (*Z. angew. Chem.*, 1906, pp. 811 and 861; Le Blanc and Nüranen (*Z. Elektrochem.*, 1906, p. 541); Förster and Koch (*Z. angew. Chem.*, 1908, pp. 2161 and 2209); Raschig (*ibid.*, 1905, 1281); Graef and Russ (*Chem. Centr.*, 1907, i. p. 1172); Warburg and Leithäuser (*Ann. Physik*, xxviii. p. 313 *Chem. Centr.*, 1907, i. 1173; 1908, i. 922).

p. 251. *Absorption of the Electrolytically Produced Nitrogen Oxides*.—The German patents of Schlarb are 273839 and 243892. Instead of Amer. P. appl. 2427 of 1911 it should be Austr. P. appl.

p. 252. Further patents on this subject: Salpetersäure-Industriegesellschaft-Gelsenkirchen (Ger. Ps. 244840 and 246712).

Amer. P. 1057977 of Pauling, assigned to the same firm; Farbwerke Höchst (Ger. P. 249329); Schloesing (Fr. P. 441607); Société Norvégienne de l'Azote et de Forces Hydro-Electriques (Fr. P. 442514); Electrochemische Werke (Fr. P. 441706).

Kroczeck, in *Oesterr. Chem. Zeit.*, 1912, pp. 266 *et seq.*, makes a survey of the hitherto-worked-out processes for the fixation of atmospheric nitrogen.

p. 257. *Nitric Acid made from Ammonia*.—Meneghini (*Gazz. Chim. Ital.*, 1912, xlii. p. 126; *J. Soc. Chem. Ind.*, 1912, p. 383) describes his experiments on the catalytic oxidation of ammonia mixed with air.

The Oest. Verein f. chem. u. metall. Produktion, Aussig (Aust. P. appl. A9851) employs a flat platinum contact body, heated to red heat, placed halfway up a perpendicular pipe through which the gases are conducted from the top downwards.

Reinders and Cats (*Chem. Weesblad*, ix. p. 47; *Abstr. Amer. Chem. Soc.*, 1912, p. 3234) studied the conditions of transforming ammonia into nitrogen oxides in the laboratory.

*Oxidation of Ammonia into Nitrogen Acids*.—Jones, Morton, Terzier, and the Semet Solvay Company (Amer. P. 1037261) oxidise a mixture of 1 vol  $\text{NH}_3$  with 2 to 2.2 vol  $\text{O}_2$  practically completely at a temperature of  $700^\circ$  to  $750^\circ$  by means of magnesium plumbate as catalyser. They employ an iron cylinder, lined with asbestos, coated with a thin layer of the contact substance, and then filled with the same. The catalyser is prepared by heating a mixture of plumbic oxide with its equivalent of magnesia from four to six hours to about  $800^\circ$  in contact with air.

p. 259. *Recovering Nitric Acid from its Mixture with Kieselguhr*.—According to Hall's B. P. 11245 of 1911, the material is placed on a grate within a tower, which is heated on the outside; a current of hot air, dried by sulphuric acid, is passed in from the top downwards, or *vice versa*. His B. P. 21724 of 1911 prescribes intimately mixing the mixture of kieselguhr, and nitric acid with sulphuric acid, which promotes the conveyance of heat into the interior of the mass during distillation and retains any water present or newly formed. After distilling off the nitric acid, both the sulphuric acid and

the kieselguhr can be recovered by treating with water; the sulphuric acid must, of course, be reconcentrated. According to his B. P. 19965 of 1911, the distillation is carried out in a retort with inclined bottom, and an outlet through which the dry kieselguhr can easily pass. By means of perpendicular horizontal, or serpentine rods or pipes, the heat is transferred from the outside to the interior. An outside jacket allows the gases to gyrate round the retort.

p. 261. *Analysis of Nitric Acid*.—For the testing of nitric acid and its impurities we refer to Lunge's *Technical Methods of Chemical Analysis*, edited by Keane, 1909, vol. i. pp. 323 *et seq.*

Fischer and Steinbach (*Z. anorg. Chem.*, 1912, lxxviii. p. 134, *Abstr. Chem. Soc.*, 1912, ii. p. 1093) describe a method for estimating nitric acid in the presence of nitrous acid, founded on the rapid esterification of nitric acid, in which oxidation to nitric acid does not take place.

Corvazier (*Abstr. Chem. Soc.*, 1912, lxxviii. p. 133) applies electric conduction to the analysis of mixtures of sulphuric and nitric acid.

p. 276. *Testing of Liquid Sulphur Dioxide*.—This article sometimes contains sulphuric acid up to 20 per cent., and it should therefore be tested in the same way as solutions of sulphur dioxide. This also holds good of the liquids prepared for the manufacture of *sulphite-paper-pulp*.

p. 278. *Modifications of Sulphur Trioxide*.—Lichty (*J. Amer. Chem. Soc.*, 1912, xxxiv. p. 1440) has examined the various modifications of this compound. The  $\alpha$ -modification, prepared by repeated distillation over phosphorus pentoxide in vacuo fuses at  $16^{\circ}\cdot79$ ; its boiling-point at pressures of 740.7 to 744.5 mm. is  $44^{\circ}\cdot23$  to  $44^{\circ}\cdot36$ , corresponding to a boiling-point of  $44^{\circ}\cdot88$  at a pressure of 760 mm. The sp. gr. was 1.9457 at  $11^{\circ}\cdot8$  and 1.7921 at  $48^{\circ}$ ; the coefficient of expansion 0.000676 at  $11^{\circ}\cdot5$ , and 0.002805 at  $40^{\circ}$  to  $48^{\circ}$ . Nowhere between  $11^{\circ}$  and  $45^{\circ}$  the volume contraction was observed which Schenck (*Annalen*, cccxvi. p. 1) asserts to take place at  $35^{\circ}$ . Another modification of  $\text{SO}_3$ , designated as the  $\beta$ -form, is the ordinary

solid product, whose molecular weight is the same as the liquid  $\alpha$ -modification, viz. = 80.

p. 279. *Decomposition of Sulphur Trioxide by Heat.*—Bodenstein and Kranendieck (*Z. physik. Chem.*, lxxx. p. 148, 1912) measured the velocity of the decomposition of  $\text{SO}_3$  in contact with quartz glass at various temperatures.

p. 303. *Specific Gravities of Sulphuric Acid.*—H. C. Moore (*J. Ind. and Eng. Chem.*, 1912, p. 677) describes a slide-rule for reducing the specific gravities of sulphuric acids of various densities and temperatures to the density of  $50^\circ \text{Bé}$ . at  $60^\circ \text{F}$ .

p. 320. *Action of Boiling Sulphuric Acid on Platinum.*—Le Roy M'Cay (*Abst. Amer. Chem. Soc.*, 1912, p. 3242) finds that the solvent action is prevented by the presence of reducing substances such as C, S,  $\text{As}_2\text{O}_3$ , and  $\text{Sn}_2\text{S}_3$ , and concludes that atmospheric oxygen or oxygen liberated by the dissociation of sulphuric acid is instrumental in causing the attack upon platinum; the preventive action of arsenious oxide and other reducing agents being due to their union with and removal of oxygen.

p. 349. "*Blue Acid.*"—On this product, formed by the action of reducing-agents on nitrososulphuric acid, further investigations have been made by Manchot (*Z. angew. Chem.*, 1910, p. 2112; 1911, p. 13; 1912, p. 1055), and Raschig (*ibid.*, 1910, p. 2248).

p. 365. *Analysis of Fuming O.V.*—Prats (*Trans. 8th Int. Congr. Appl. Chem.*) weighs off 6 g. of the O.V. in a small glass-bulb, dissolves in 1 litre of water, and titrates 250 c.c. of this solution with standard caustic soda solution and methyl-orange; the number of cubic centimetre soda solution used =  $a$ . Another 250 c.c. is titrated with decinormal iodine solution =  $b$ . The total quantity of  $\text{SO}_3$  ( $k$ ) =  $\frac{4(20a - b)}{55}$ , that of  $\text{SO}_2$  ( $l$ ) =  $\frac{28b}{5}$ ; the total water ( $u$ ) =  $100 - \frac{16a + 0.48b}{5}$ ; the combined



$\text{SO}_3 = 4.44 u$  and altogether:

$$\text{Per cent. H}_2\text{SO}_4 = u + 4.44u = 5.44u \times \frac{49}{9} \left( 100 - \frac{16a + 0.48b}{s} \right)$$

$$\therefore \text{ free SO}_3 = r - \frac{10u}{9} = \frac{4}{9} \left( \frac{196a + 3b}{s} - 1000 \right)$$

" "  $\text{SO}_2 = t$ .

Knorr (*Chem. Zeit.*, 1912, p. 1262) estimates the total  $\text{SO}_3$  in one sample of the O.V. gravimetrically, and in another sample the  $\text{SO}_2$  by titrating with iodine. He performs the weighings according to Lunge's prescription (*suprà*, p. 359) in a glass-bulb drawn out into a capillary which is thrown into a boiling solution of barium chloride, acidulated with hydrogen chloride. The barium sulphate is separated and estimated in the usual way.

p. 374. *Diphenylamine as Reagent for Nitrogen Acids.*—According to Iwanow (*Chem. Zeit.*, 1912, p. 1170) fuming O.V. completely free from nitric acid is coloured by diphenylamine, if it contains more than 20 per cent.  $\text{SO}_3$  and the temperature rises above  $70^\circ$ , as will happen when carrying out the reaction in the way indicated in the text. With fuming O.V. of 30 per cent.  $\text{SO}_3$  the temperature rises up to  $110^\circ$ . At  $70^\circ$  the colour produced is red; at higher temperatures it passes into purple and then into blue. This can be avoided by mixing the O.V. if it contains about 30 per cent.  $\text{SO}_3$  with 20 c.c. of chemically pure sulphuric acid of sp. gr. 1.84, whereby a mixture of nearly the formula  $\text{H}_2\text{SO}_4$  is formed; this is cooled down to nearly the ordinary temperature, 1 c.c. diphenylamine solution is added, well shaken up, and allowed to stand for one minute. If then no colour has appeared no nitric acid is present.

p. 389. *Analysis of Nitrous Nitriol.*—Corvazier (*Monit. Scient.*, 1912, p. 322) describes a method for estimating the nitrous acid by means of the electric conductivity.

p. 390. *Detection and Estimation of Small Quantities of Nitrous Acid.*—E. Holl Müller (*Analyst*, xxxvii. p. 345) employs a solution of 8 g. dimethylaniline and 4 g. hydrochloric acid in 100 c.c. water, of which he adds 3 drops together with 1 drop

of hydrochloric acid to 50 c.c. of the solution to be examined. In fifteen to thirty minutes a yellow colour, due to  $\beta$ -nitrosodimethylaniline, is developed. This is matched in a colorimeter, with the colour developed by using known amounts of a sodium nitrate solution containing 1 part  $\text{HNO}_2$  per 100,000. The presence of nitrates does not interfere, and the reaction will detect 1 part  $\text{HNO}_2$  per 1,000,000.

p. 413. *New Brimstone Burners*.—Hunt (B. P. 18895 of 1911) provides for the brimstone burners a self-acting contrivance for the introduction of air. From the main air-pipe a pipe is branched off leading directly into the combustion chamber, which contains a thermostat for regulating the air-valve.

H. H. Niedenführ (Ger. P. 249330) avoids the subliming of sulphur and the formation of  $\text{SO}_3$  by special contrivances. Cf. *infra* his process for treating the burner-gases.

Rossiter (Amer. Ps. 1038442 and 1039812) employs for burning brimstone a revolving drum, with a gas outlet at one of the ends, connected with an aspirator. Within that drum there is an inner drum connected with it for revolving; here the sulphur is burned. The annular space between both drums receives the heat radiated from the inner drum. The latter is provided with air inlets and with gas outlets, passing into the annular space, where more air is introduced in order to burn the subliming sulphur.

H. B. P. Humphries (B. P. 11750 of 1912) divides the burner by means of a plate into an upper and lower chamber connected by a narrow passage in the plate. The latter is made hollow to permit of the circulation of cooling-water. The sulphur is burnt in a circular tray in the bottom chamber, the air for this purpose being heated up by circulating round the tray.

The plate between the two chambers is also cooled by air, which afterwards serves for burning the sulphur subliming into the upper chamber. The sulphur is charged by means of a hopper passing through the upper chamber and the plate into the bottom chamber.

Another automatic sulphur-burner, is described in the Amer. P. 1044369 of G. W. Fortier, assignor to E. B. Berwick.

p. 501. *Mechanical Pyrites-burners*.—Further modifications: Scherfenberg, Ger. P. 251038; Renwick, Ger. P. 246180; Erzröstgesellschaft Köln, Ger. P. 246087; Parent, B. P. 28078 of 1911.

p. 504 *Roasting of Blende*.—A detailed discussion of the principles of blende roasting is published by W. Hommel in *Metallurgie*, 1912, pp. 281-296. We shall make use of it in the following notes:—

p. 507. According to Hommel (*loc. cit.*) a Rhenania furnace when worked with two shifts gets through 6.5 tons, with three shifts to 9 tons. In the first case the ore takes fifty to sixty hours to get through the furnace, but only during a tenth of this time it is actually stirred, all the other time it lies still, and only at the top the sulphur is burning off. This drawback is particularly noticed in the case of blende containing lead. In the bottom muffle in the same time four or five times as much sulphur is removed as in the top muffle, partly owing to the higher temperature, partly to the fact that the bottom muffle receives fresh air, and the muffles above it are already charged with  $\text{SO}_2$ . Hommel therefore objects to the Rhenania furnaces.

p. 508. *Mechanical Blende-roasting Furnaces*.—Enumerations of the various descriptions of such furnaces are given by Schütz in *Metallurgie*, 1911, pp. 635 *et seq.*; and by Hommel, *loc. cit.*, pp. 290 *et seq.* The latter divides them into two classes, viz., those where the hearth itself is moving, and those provided with moving stirrers. The first class comprises: (a) horizontal revolving drums; (b) vertical revolving furnaces. The second class: (a) long furnaces with one or more floors in which the stirrers travel horizontally lengthways; (b) furnaces with revolving stirrers. A combination of these two classes is Hommel's furnace, (Ger. P. 204423) in which the first roasting of the ore takes place in a revolving hearth, and the desulphurisation is completed on a fixed annular hearth in which the ore is moved forward by stirrers attached to the periphery of the revolving hearth.

1. *Revolving Drums*.—According to Hommel only one furnace of this class has up to now been carried out in actual

practice, viz., that constructed by Köhler at Lipine (Silesia), in a very ingenious way, but the quantity of ore got through is too small. Another such furnace, by Daniel and Römer (Ger. P. 208354), consisting of a number of small drums, has not yet been proved successful on a working scale.

Schmieder (Ger. P. 244131) describes such a furnace provided with special arrangements for the preheating of the air.

2. *Revolving-Hearth Furnaces*.—These furnaces have horizontal hearths and a vertical axis. The stuff passes the hearths radially from the centre to the circumference, and *vice versa*, so that its transit through the furnace is approximately a spiral course. According to Hommel (*loc. cit.*, p. 290) it is the best of all systems, both in respect of the smaller expense of plant and repairs, and of the consumption of coal and regularity of work. Furnaces getting through 50 tons *per diem* require only one h.-p. The application of this system to muffle-furnaces, with indirect heating of the revolving hearth, presents some difficulties. The fireplace may be either fixed on the outside or revolve together with the hearth. The air for roasting is best introduced at the circumference, and the roasting-gases taken out in the centre, thus obtaining a gas rich in  $\text{SO}_2$ , and fully utilising its heat for preheating the fresh ore. The sole is best shaped as a plate of a pretty large surface, say 26 to 33 ft. diameter, which certainly requires a very high covering-arch. Such furnaces cannot be used for the complete roasting of the ore, but only for the first roasting; but they are easily combined with a fixed hearth on which the dead-roasting is performed. As long as the ore still contains enough sulphur, the roasting-process goes on more favourably in this class of furnaces than in those with revolving scrapers.

Such furnaces, where the fireplace revolves together with the hearth, are described in Zelewski's Ger. P. 142435, and Trego (Amer. P. 798844).

Hommel's Ger. P. 204423 describes a furnace with revolving plate-hearth on which the ore is turned by means of air which had been preheated by cooling the plate. This plate is constructed as an arch, whereby an excessive height of the roof-arch is avoided. The desulphurisation is completed in a stationary ring-furnace. Another furnace of Hommel's possesses an arched plate, heated by producer-gas from below when

used for lead or copper ores; for pyrites it requires no external heating.

3. *Long Furnaces with Straight-lined Stirrers.*—The scrapers are fixed to a transverse piece running on rollers attached to both sides of the furnace, and removed from time to time to be cooled outside. The hearths must, as Hommel reports, be made very long, e.g., 330 ft. in Saeger & Brown's furnace, which for all that get only through 10 tons in twenty-four hours with great consumption of coal. (I myself saw a furnace of this class, by Hegeler, at work at the inventor's factory at La Salle, Ill., which got through 35 to 40 tons blende on 28 per cent. in twenty-four hours.) Mühlhäuser (*Z. angew. Chem.*, 1910, p. 347) gives a detailed description of Hegeler's furnace (Amer. Ps. 303531 and 592006), and Hommel (*loc. cit.*, p. 292) describes a Hegeler furnace containing seven muffles of a total length of 524 ft., a horizontal area of 295 × 19.7 ft. and 19.7 ft. high, but not at all working with a success corresponding to these colossal dimensions.

To this class belong also the Ger. P. 61043 of the Chemische Fabrik Rhenania, and of Encke, No. 211433.

4. *Furnaces with Revolving Stirrers.*—To this class belong the furnaces for roasting pyrites-smalls, constructed by MacDougal, Frasch, Herreshoff, and others, described *suprà*, pp. 474 *et seq.* They have been very successful for treating ores rich in sulphur, but less so for blende and other poor ores.

Other furnaces have been specially constructed for blende, such as the furnaces of Haas (*suprà*, p. 508), of the Société Vieille Montagne (*ibid.*), of Zellweger (*Eng. and Min. J.*, 1900, p. 301), of O'Brien (*suprà*, pp. 497, 509), of Zelewski (Ger. Ps. 195724 and 201191), of Merton and Ridge (B. Ps. 13625 of 1909; 3843 and 3581 of 1911).

Hommel (*loc. cit.*, pp. 294 *et seq.*) gives a comparative criticism on the most important systems of mechanical blende-roasting. Other reports of this kind have been made by Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1291), Schütz (*Metallurgie*, 1911, p. 637); Nemes (*ibid.*, 1912, p. 516).

p. 512. *Prescriptions for Roasting Blende.*—Further communications on this subject have been made by Thomas

(*Metallurgie*, 1910, parts 9 and 10); Mostowitch (*Chem. Zeit. Rep.*, 1911, p. 763); Hofmann (*Trans. Amer. Inst. Min. Eng.*, 1904, p. 834).

p. 512. *Testing of the Cinders from Roasting Blende*.—Prescriptions for this are found in Lunge's *Technical Methods of Chemical Analysis*, edited by Keane, vol. i., part 1, p. 298.

Nitchie (*J. Ind. Eng. Chem.*, 1912, p. 30) heats a sample of the cinders to 1000°, preferably in a boat, placed in an electrically heated tube, in a current of air free from CO<sub>2</sub>, absorbing the sulphur oxides formed in standard caustic-soda solution and retitrating the excess of this, employing phenolphthalein as indicator. This process (which is *not* applicable to fresh ore!) takes less than ten minutes. The sulphur existing in the form of calcium sulphate, which is not driven out by the air-current, can be approximately calculated from the calcium contents of the ore.

p. 514. *Treating Complex Sulphur Ores yielding Poor Gases*.—Further processes for this purpose have been proposed by Nemes (Fr. P. 426851); Renwick (Amer. P. 981880); Grünwald and Welsch (Ger. Ps. 232044 and 238293); Aktiengesellschaft für Bergbau, Blei- und Zinkfabrikation zu Stolberg (Ger. P. 253492).

*Roasting of Lead Ores in "Converters" by the Process of Huntington and Heberlein*.—The theory of this process is discussed by Bannister in *Inst. Min. and Metall.*, 1912, 8th February; abstracted in *J. Soc. Chem. Ind.*, 1912, p. 285.

p. 515. *Sulphuric Acid from the Gases of Sulphide Ores*.—In Laney's report (U.S. Geol. Survey, quoted from *Chem. Ind.*, 1913, p. 11) the enormous chamber plants of some American mining companies are described. The Tennessee Copper Company work up about 400,000 tons of sulphide ores per annum in seven large blast furnaces, and now produce 180,000 to 200,000 tons acid 60° Bé. per annum. The plant comprises two octagonal Glover-towers 50 ft. high and 30 ft. diameter, sixty-four chambers of 50 x 50 x 70 ft., and eight chambers of 32 x 50 x 80 ft.; ten Gay-Lussacs of 20 to 36 ft. diameter, and 50, to 70 ft. high, etc., etc. The Ducktown Sulphur, Copper, and Iron Company produces

160 to 200 tons acid of 60° Bé. per diem. The ore contains 14 to 19 per cent. S.

p. 517. *Burning Spent Oxide of Gas-works.*—The Chemische Industrie Aktien Gesellschaft and F. Wolf (Ger. P. 248001) recover all the sulphur liberated in the distillation of coal by mixing the  $\text{SO}_2$  gas obtained by burning the spent oxide with the waste gases of the furnace, whereby the sulphur dioxide contained in these gases is equally utilised.

p. 521. *Dealing with the  $\text{SO}_2$  contained in Smoke-gases.*—Wislicenus discusses the damage caused by smoke-gases and his process for preventing it in a pamphlet: "Über die Abgasfrage, etc.," 1912, and several papers published in 1910 and 1911. His apparatus, called "dissipator," is protected by B. P. 16609 of 1908; Amer. P. 988920; Ger. Ps. 228922 and 229070; Swiss P. 44774; Fr. P. 397953; Belg. P. 212930; Norw. P. 19003; Austr. P. 45391.

p. 524. *Absorbing the  $\text{SO}_2$  contained in Smoke-gases.*—Wedge (Amer. P. 1039464) describes a tower constructed for this purpose.

p. 531.  *$\text{SO}_2$  from the Waste Liquor of the Manufacture of Sulphite Paper-pulp* is recovered by Achenbach (Ger. P. 252412) by atomising the liquor into a thin mist in a closed receptacle by means of its own pressure, whereby  $\text{SO}_2$  is set free.

p. 533. *Manufacture of Liquid Sulphur Dioxide.*—Blanc (Amer. P. 1034574) cools and dries the gas, removing suspended solid particles, passes it through a mixture of glycerin and an alkaline solution, and cools it down again.

Moulin and Vandini (Fr. P. 432431), Burbury (Fr. P. 420596), describe apparatus for the manufacture of liquid sulphur dioxide.

Pacottet (Fr. P. 365224) describes an apparatus called "sulphitometer" for measuring off liquid sulphur dioxide.

H. H. Niedenführ (Ger. Ps. 254044 and 254362) obtains from purified and cooled roasting-gases liquid sulphur dioxide at a comparatively low pressure by strong cooling in a vacuum.

p. 540. *Carriage of Liquid Sulphur Dioxide*.—The Heylands Company (Ger. P. 250263) construct vessels for keeping and carrying liquefied gases, consisting of two concentrically arranged metallic vessels, with a specially arranged shape of the thin neck of the inside vessel.

p. 543. *The purification of sulphurous-acid gas for the destruction of vermin*, etc., is treated in the Amer. P. 1034574 of Blanc.

p. 553. *Purification of the Burner-gases from Flue-dust*.—Wright (*Eng. and Min. J.*, 1910, xc. p. 111) found in the gases from pyrites-burners which had passed through a small dust-chamber with a velocity of 1 ft. per second, 0.28 g. solid particles per cubic metre, and after passing through a wash-tower and a long pipe still 0.11 g.

Asbrand (Ger. P. 243787) describes a centrifugal apparatus for the removal of flue-dust.

Other patents in this direction: Beth, Ger. P. 245569; Michaelis, Ger. P. 244206; Maschinenfabrik Buckau, Ger. P. 245319.

p. 555. *Sublimed sulphur contained in burner-gases* is removed, according to H. H. Nüdenführ's Ger. P. 249330, by passing the gases together with an excess of heated air through hot metallic pipes. It is also suggested to construct the grates of the pyrites-burners of pipes through which the mixture of burner-gases and air is passed.

p. 555. *Purification of Burner-gases*.—Girod (B. P. 17157 of 1910) removes arsenic, etc., by thorough filtration of the gases between the burners and the Glover through several boxes, packed with granite, or lava, or other acid-resisting materials in pieces of various degrees of fineness, and then passing the gases through washing-towers fed with sulphuric acid of 30° to 40° Bé. The nitrous vitriol coming from the Glover-tower is treated with nitric acid, in order to oxidise the arsenious acid to arsenic acid which is partly retained in the Glover, and completely in washing-towers following upon this. The acid from the latter goes through the Glovers.



Blanc (Amer. P. 1034574) describes an arrangement for purifying sulphurous gases destined for destroying vermin.

p. 573. *A modification of the Reich apparatus* for estimating the sulphur dioxide in burner-gases, etc., is described by Ljungh in *Chem. Zeit.*, 1909, xxxiii. p. 143.

p. 578. *Estimation of Total Acids in Burner-gases.*—Lunge (*Z. angew. Chem.*, 1890, p. 567) has proposed applying for this purpose a continuous estimation of the specific gravity of the gases by the Lux gas-balance or other technical gas-balances. This proposal does not appear to have met with any application for manufacturing purposes.

p. 579. *Various modifications of the Orsat apparatus* are described by Dennis (*J. Ind. and Engin. Chem.*, 1912, p. 898).

p. 588. *Wrought-iron for chamber-pillars*, etc., is extensively employed in the system of Moritz, *suprà*, p. 614.

p. 605. *Horizontally arranged straps for suspending the side-sheets of lead-chambers* are recommended, in preference to perpendicular straps by Awe (*Z. angew. Chem.*, 1912, p. 2523).

p. 615. *The Moritz system of building lead-chambers* is favourably reported on by F. H. Norton (*J. Ind. and Engin. Chem.*, 1912, p. 532). The cost of building is 33 per cent. higher than that of the ordinary system; 1 cb.m. of chamber space at Stettin makes 7 kg. acid of 50° Bé., with a consumption of 0.5 kg. nitric acid of 30° Bé. per 100° sulphuric acid.

Another French patent of Moritz (No. 444474) states that his chambers are preferably circular in section, or square with rounded corners.

p. 627. *Shape of Lead-chambers.*—Wentzki (Ger. P. 238739) employs cylindrical chambers fitted with mechanical contrivances.

p. 651. *Diminishing the Chamber-space.*—Meigs (Amer. P. 1022493) arranges inside the chamber a hollow, rhomboidal

"deflector" reaching from top to bottom, but at some distance from the sides. At the side where the gases enter, the deflector is concave. By this arrangement the gases during their passage through the chambers are alternately compressed and expanded.

p. 692. *Tower Processes for Manufacturing Sulphuric Acid.*—The discussion on the Opl process is continued by Hartmann (*Z. angew. Chem.*, 1912, p. 817) and Meyer (*ibid.*, p. 1426).

According to the English Alkali Inspectors' Report for 1911 (*J. Soc. Chem. Ind.*, 1912, p. 716), the Opl system had been successfully introduced at an English factory.

*Other Processes.*—Witney (Amer. P. 1022012, transferred to the General Electric Company of New York) mixes waste gases containing  $\text{SO}_2$  with steam and nitrous gases, and carries the mixture over electrodes of widely distant electric potential, whereby sulphuric acid is formed.

Pasquier (Fr. P. 441813) employs a number of vessels in which the pyrites-kiln gases, mixed with nitrous gases, pass through sulphuric acid followed by a cooling vessel. Automatic valves of special construction prevent a loss of gases.

Düron (Ger. P. appl. D26515 of 1912) describes a new tower-system for making sulphuric acid.

p. 706. *Potting the Nitre.*—For this purpose Pohl (*Z. angew. Chem.*, 1912, p. 1850) recommends pipes made of quartz-glass ("vitreosil," p. 1573), with cast-iron muffles for protecting them.

p. 723. *Introduction of Steam into the Chambers.*—Pohl (*Z. angew. Chem.*, 1912, p. 1220) does this by means of a spray-producer, whereby the gases are thoroughly mixed.

p. 738. *Introducing Liquid Water into the Chambers in the Form of Spray.*—Gazel (*Chem. Zeit. Rep.*, 1911, p. 464) states that in chambers making only 3 or 4 kg. acid of 53° Bé. per cubic metre, the employment of sprayed liquid water is only suitable in summer time and offers no great advantage; but in the "high pressure work" (p. 639) liquid water must be used in order to spare the chambers and to save nitric acid.

A new form of spray-producers has been recently constructed

by Poley, and is sold by «Rudolph Heinz, of Hanover. It is made of glass, with an inner ebonite spiral, and does the same work as a spray-producer of platinum, etc., whilst costing only one-twelfth of this; which for a chamber-plant of 10 tons pyrites per diem, for which fifteen spray-producers are required, means a considerable saving, apart from avoiding the risk of purloining, always present with apparatus made of costly metals. The fifteen Poley producers cost only 8s. 6d. each, or £6, 7s. 6d. altogether, against £75 for platinum or £45 for platinum-iridium, or £37, 10s. for gold.

p. 799. *Apparatus for recovering the Nitre*.—According to the B. P. 11452 of 1912, of Lymn, the liquid runs down upon inverted truncated cones on to the centres of revolving discs.

p. 804. *Apparatus for distributing the Acid for feeding the Towers*.—Briggs (Amer. P. 1032657, assigned to the General Chemical Company) employs a conical distributor, fluted outside, below which is a perforated disc, the holes in which correspond to the outlets of the distributor.

Fowler and Medley (B. P. 23864 of 1911) cause the liquid to run from the outside to the centre, where it is atomised by quickly revolving discs.

The apparatus of the Farbenfabriken Bayer mentioned *suprà*, p. 792, also comes under this heading.

p. 861. *Lining of Glover-towers*.—Of course the quartz-glass («vitreosil») mentioned *suprà*, p. 1123, and *infra*, p. 1573, is entirely in its place here.

p. 878. *Packing of Glover-towers*.—Moschick\* (B. P. 17355 of 1911) employs a horizontal chamber, properly packed, through which the gases pass in a horizontal direction; perforated partitions divide it into several compartments.

Vollberg (Ger. P. 247950) employs as packing, charcoal made from wooden blocks of a special shape.

Kirkham Hulett and Chandler Lim., Hersey and Blake (B. Ps. 18129 of 1908, and 23813 of 1911) employ a tower, separated into a number of compartments by horizontal

partitions, the liquid being squirted about by revolving discs or troughs.

p. 985. Any *nitrous oxide* (nitrogen protoxide,  $N_2O$ ) present in the *exit-gases* from the chambers or towers may be estimated by the methods quoted *suprà*, p. 581.

p. 1074. *Preparation of Colourless Sulphuric Acid*.—Such acid, also free from arsenic and iron, is obtained, according to Girod's B. P. 17157 of 1911, by first purifying the burner-gases mechanically, then passing them while still hot over nitrous sulphuric acid, to which a little nitric acid has been added; the nitrous sulphuric acid is afterwards denitrated, any arsenious acid present is oxidised, the gases are passed through washing-towers, and then submitted to the chamber-process.

p. 1077. *Chemically pure Sulphuric Acid*.—For distilling sulphuric acid in moderate quantities in order to prepare chemically pure acid, the Deutsche Ton- und Steinzeugwerke in Charlottenburg supply retorts made of quartz-glass ("vitrosil") holding 3 to 75 litres; the attached pipes and cooling-worms consist of the same material.

Bressanin (*Gazz. Chim. Ital.*, xlii. i. 456; *Chem. Centr.*, 1912, ii. 684) prepares absolutely pure sulphuric acid by adding hydriodic acid to sulphuric acid of 50° B $\acute{e}$ ., filtering through glass-wool or asbestos, and removing the iodine from the filtrate by heating it in vessels of glass free from arsenic.

p. 1093. *Lead-pans for Sulphuric Acid*.—Mackenzie (B. P. 2389 of 1912) employs in cascade apparatus an inner tube for promoting the circulation of the acid.

p. 1123. *Quartz-glass (Vitreosil)*.—From the paper of Pohl quoted in the text and on p. 1571, we give the following extract:—

The German firm "Deutsche Ton- und Steinzeugwerke," of Charlottenburg, has combined with the Thermal Syndicate, Limited, and founded in 1910 the "Deutsch-Englische Quarzschmelze" at Pankow, near Berlin. Pohl states the most important properties of quartz-glass as follows: It fuses between 1700° and 1800°, but softens sensibly already a little over 1500°

Its co-efficient of expansion is  $\alpha = 0.00000059$ , *i.e.*, about one-seventeenth of that of glass. It therefore resists very rapid changes of temperature without cracking. On being heated for a long time, *e.g.*, four hours to  $1350^{\circ}$ , it is devitrified and loses about half of its strength; it should, therefore, not be heated above  $1200^{\circ}$  during long time (in chemical operations this temperature is hardly ever reached). It resists nearly all acids, especially sulphuric, nitric, and hydrochloric acid, but it is acted upon by hydrogen fluoride, and above  $400^{\circ}$  also by phosphoric acid.<sup>1</sup>

Pohl describes a great number of applications of vitreosil for apparatus in chemical industry, but we mention here only his statements concerning its application for cascade apparatus in the concentration of sulphuric acid. Vitreosil dishes need not be protected against the heat of the fire by fire-proof plates. These dishes, in two or more series, hang on asbestos rings in open fire-clay rings over a fire-flue. The fuel is coke-breeze or any other cheap material; the flame nowhere comes into direct contact with the acid. The fire-gases are afterwards used for preheating the acid, in square quartz pans. The hot acid flows from the last (hottest) dish through a vitreosil pipe into a vitreosil cooler. The vapours from the dishes pass through a scrubber and then into a chimney; they contain only about 2 or 3 per cent. of the acid. Usually fifty dishes are employed in two rows, or thirty pans in three rows. Such a set produces daily 5 tons strong acid from cold acid of about  $50^{\circ}$  Bé, with an expenditure of 15 to 20 per cent. of coal. Two such sets, producing 10 tons per diem, can be placed alongside. There are also some special shapes of dishes and pans made from this material. In May 1912, thirty-eight such plants were working in England, about the same number on the Continent, and others in Canada, the United States, and Australia. Altogether there are now 5000 dishes in daily use, producing 170,000 tons sulphuric acid of  $65^{\circ} \cdot 7$  Bé. per annum.

*Siloxide*.—This is the designation of quartz-glass, containing zirconia and titanium, patented by Wolf-Burkhard as B. P. 180533 of 1911, described by Felix Thomas in *Chem. Zeit.* of 9th January 1912. Pohl (*loc. cit.*) contests its advantage over vitreosil.

<sup>1</sup> Bodenstein and Krauendieck (*Z. physik. Chem.*, 1912, lxxx. p. 146) investigated the velocity of the decomposition of sulphuric acid in contact with hot quartz-glass.

which is stoutly maintained by the Zirkonglassgesellschaft of Frankfurt, in *Z. angew. Chem.*, 1912, p. 2349.

p. 1129. *Cascade Apparatus for the Concentration of Sulphuric Acid*.—Such apparatus has been also composed of "Field" tubes as they are employed in connection with steam-boilers, in this case made of quartz-glass or of "tantiron" (vide *infra*), and supported at their upper shoulder and at the bottom by specially shaped "gibsonite" blocks. A B. P. 2389 of 1912 of Mackenzie, has been taken out for it. Such a cascade is shown in *Chem. Trade J.*, 1912, li. p. 459.

p. 1153. *Price of Platinum*.—According to Mansch (*Deutsche Technik*, 1912, p. 456), the price of platinum in 1912 was £9, 5s. per oz. The Ural district in 1910 still furnished 281,000 oz., but the principal deposits of that district were exhausted.

p. 1209. *Concentration of Sulphuric Acid by Hot Air*.—Girod (B. P. 17158 of 1911) concentrates the acid first in lead pans at 150° to 160° C., and then exposes it in a finely divided state to the simultaneous influence of hot air and low pressure.

p. 1217. *Monohydrated Sulphuric Acid*.—Duron (Fr. P. 430145) prepares this by enriching ordinary concentrated sulphuric acid with  $\text{SO}_3$ , formed by the dissociation of part of the acid circulating in the process into  $\text{SO}_3$  and  $\text{H}_2\text{O}$ . The water formed at the same time is taken up by  $\text{SO}_3$ , formed from another portion of the circulating acid, and is removed by reconcentration. All of this is brought about by a current of highly heated air.

p. 1326. *Theory of the Contact-processes for the Manufacture of Fuming Q.V.*—A. E. Lange (*Z. Ver. deut. Zuckerind.*, 1912, p. 355) shows that sugar is a negative catalyser, which may reduce the amount of  $\text{SO}_3$ , catalytically formed from  $\text{SO}_2$  by cupric sulphate, to half or even one-ninth of that otherwise obtained.

p. 1400. *The Schroeder-Grillo Process for the Catalytic Manufacture of Sulphuric Acid*.—Patterson and Cheney (*J. Ind.*

and *Eng. Chem.*, 1912, pp. 723 *et seq.*) describe the plant erected in the U.S. Naval Proving Ground, Indian Head, Ma., by the New Jersey Zinc Company. There native Louisiana sulphur is burnt, and 6 tons acid of 98 per cent. is made *per diem*. The burner-gas enters the converter with a temperature of  $380^{\circ}$ ; the rate of conversion is 95 to 95.5 per cent. The gas on entering the contact-apparatus contains 6.5 to 7 per cent.  $\text{SO}_2$ . The consumption of coal is 21.8 parts to 100  $\text{SO}_3$  produced; the average yield is 93.36 per cent. of that calculated from the S burnt. At first they worked with pyrites; by going over to brimstone the cost of 98 per cent. sulphuric acid has been reduced nearly by 2\$, partly by saving in repairs, partly by increasing the yield, and by a smaller consumption of coal.

p. 1428. *Contact-apparatus*.—Grosvenor, Amer. Ps. 1086609 and 1036610; Eschelmann, Harmuth, and the General Chemical Company, Amer. P. 1036473.

p. 1432. *Contact-substances*.—According to Messel (*Chem. Trade J.*, 1912, li. 237) the loss of platinum in the contact-process averages 1 grain per ton of the sulphuric acid produced. This loss can only take place mechanically, and can be proved in the drip tubes, although the platinum cannot be discovered in the gases on account of the enormous dilution.

p. 1441. *Combination of the Contact-process and the Chamber-process*.—Wilde (8th Int. Cong. Appl. Chem., 1912, ii. 249; *Abstr. in J. Soc. Chem. Ind.*, 1912, p. 876) passes the pyrites-burner gases into a shaft, filled with ferric oxide contact-mass, where about 30 per cent. of the  $\text{SO}_2$  is converted into  $\text{SO}_3$ , and then by means of a fan-blast through a Glover-tower and into lead-chambers. By this combination the work done by the chambers is increased at least by 30 per cent.; more uniform results are obtained, and 30 per cent. of the nitre is saved. All the acid can be brought in the Glover to  $60^{\circ}$  B $\phi$  and upwards, and can be obtained colourless. The ferric oxide removes also 95 per cent. of any arsenic present, and at the same time acts as a dust-catcher.

p. 1441. *Formule for preparing Fuming Oil of Vitriol of Definite Percentage of Sulphuric Anhydride*.—Prats (*Verh. Int. Kongr. f. angew. Chem.*, 1912) gives the following formulæ for this object:—

$$1. \quad x = a \times \frac{9h + 40(100 - s)}{9k + 40(100 - s)}$$

$$2. \quad y = a - x = a \times \frac{9(k - h)}{9k + 40(100 - s)}$$

$a$  means the quantity of fuming O.V. to be prepared, containing  $h$  per cent. of free  $\text{SO}_3$ .

$x$  is the weight of the fuming O.V. to be employed, containing  $k$  per cent. free  $\text{SO}_3$ .

$y$  is the weight of ordinary sulphuric acid with  $s$  per cent.  $\text{H}_2\text{SO}_4$ , to be mixed with the preceding.

If, as is the usual case, ordinary acid of  $66^\circ \text{Bé.}$  is employed, the following abridged formulæ can be used:—

$$3. \quad x = a \times \frac{h + 20}{k + 20}$$

$$4. \quad y = a \times \frac{k - h}{k + 20}$$

p. 1459. *Working Pyrites-cinders for Iron in Blast-furnaces*.—Simmersbach and Schulz (*Stahl u. Eisen*, xxxii. 1254) describe troubles caused by this process. Apart from making the slags highly basic, the temperature in the fusing zone must be kept as high as possible, in order to sufficiently desulphurise the pig-iron. The quantity of the slag is also important. A high percentage of  $\text{CaS}$  in the materials charged does not considerably increase the fusing-point of the slag formed.

p. 1470. *Selenium*.—The application of this for colouring sodium-calcium glasses is discussed by Ferrardi (*Chem. Zeit.*, 1912, p. 1149).





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